PB82-247354

Methodology for Overland and Instream Migration and Risk Assessment of Pesticides

Battelle Pacific Northwest Labs.
Richland, WA

Prepared for

Environmental Research Lab.
Athens, GA

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Athens GA 30613

EPA-600/3-82-024
May 1982

PB82-247354

Research and Development

EPA

Neg. Sample
P.O. 3401
g 22761

Methodology for Overland and Instream Migration and Risk Assessment of Pesticides

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-82-024	2. Applications Guide	3. RECIPIENT'S ACCESSION NO. PB82-247354
4. TITLE AND SUBTITLE Methodology for Overland and Instream Migration and Risk Assessment of Pesticides		5. REPORT DATE April 1982
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Y. Onishi, S.M. Brown, A.R. Olsen, M.A. Parkhurst, S.E. Wise, and W.H. Walters		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Pacific Northwest Laboratories Richland Washington 99352		10. PROGRAM ELEMENT NO. AARB1A
		11. CONTRACT/GRANT NO. 68-03-2613
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory--Athens GA Office of Research and Development U.S. Environmental Protection Agency Athens, Georgia 30613		13. TYPE OF REPORT AND PERIOD COVERED Final, 4/78-1/80
		14. SPONSORING AGENCY CODE EPA/600/01
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

To provide planners and decision makers in government and industry with a sound basis for decision making, the Chemical Migration and Risk Assessment (CMRA) Methodology was developed to predict the occurrence and duration of pesticide concentrations in surface waters receiving runoff from agricultural lands and to assess potential acute and chronic damages to aquatic biota. The CMRA Methodology consists of overland pesticide transport modeling, instream pesticide transport modeling, statistical analysis of instream pesticide concentrations, and risk assessment. The CMRA methodology uses the state-of-the-art overland and instream models ARM and SERATRA to continuously simulate nonpoint source pollution processes. It is useful for evaluating both short and long-term migration and fate of both dissolved and particulate pesticides. The risk assessment procedure, coupled with the statistical analysis of predicted instream pesticide concentrations by the computer program FRANCO, and pesticide toxicity data provides a good scientific basis for pesticide risk assessment. Because of a lack of extensive knowledge on pesticide toxicity, however, the risk assessment procedure includes only the direct effects of dissolved pesticide concentrations on aquatic biota. The risk assessment does not include ingestion effects or any indirect effects such as bioconcentration and biomagnification. The methodology is general enough to handle heavy metals, radionuclides, and other toxic contaminants as well.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 220
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/3-82-024
May 1982

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Contract No. 68-03-2613

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management and engineering tools to help pollution control officials achieve water quality goals through watershed management.

Many toxic contaminants are persistent and undergo complex interactions in the environment. As an aid to environmental decision-makers, the modeling technique described in this report was developed to simulate overland and instream transport of toxic contaminants and to predict the probability of acute and chronic impacts on aquatic biota.

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ABSTRACT

To provide planners and decision makers in government and industry with a sound basis for environmental decision making, the Chemical Migration and Risk Assessment (CMRA) Methodology was developed to predict the occurrence and duration of pesticide concentrations in surface waters receiving runoff from agricultural lands and to assess potential acute and chronic damages to aquatic biota. The CMRA methodology consists of overland pesticide transport modeling, instream pesticide transport modeling, statistical analysis of instream pesticide concentrations, and risk assessment.

The CMRA Methodology uses two state-of-the-art overland and instream models, ARM and SERATRA, to continuously simulate nonpoint source pollution processes. It is useful for evaluating both short- and long-term migration and fate of both dissolved and particulate pesticides. The risk assessment procedure, coupled with statistical analysis of predicted pesticide concentrations by the computer program FRANCO and pesticide toxicity data, provides a good scientific basis for pesticide risk assessment. Because of a lack of extensive knowledge on pesticide toxicity, however, the risk assessment procedure includes only the direct effects of dissolved pesticide concentrations on aquatic biota. The risk assessment does not include ingestion effects or any indirect effects such as bioconcentration or biomagnification. In addition to pesticides, the methodology is general enough to handle heavy metals, radionuclides, and other toxic contaminants.

To examine its applicability and limitations, the CMRA Methodology was applied to the Four Mile Creek Watershed (Iowa), including Four Mile Creek and Wolf Creek, to evaluate migration and fate of the pesticide alachlor, and its potential acute and chronic impacts on different fish species. A risk assessment was also performed for the pesticide toxaphene. The study demonstrated that the CMRA Methodology is capable of predicting fate and effects of pesticides for a wide range of compounds, agricultural lands, receiving streams, and aquatic biota. The methodology needs additional testing, however, to confirm its validity. One of the shortcomings of the methodology is that it requires extensive field and laboratory data and that it may be limited by the availability of required data.

Aside form its direct use by government and industry to assess the impacts of pesticide practices, this methodology will also provide researchers with a way to evaluate the relative importance of various mechanisms that control transport and fate phenomena occurring on watersheds and in receiving streams, as well as a way to investigate the effectiveness of alternative land management and pesticide control policies.

After development of the CMRA Methodology, the feasibility of fitting overland and instream pesticide concentrations with statistical distributions was examined. This task was conducted to determine whether a simpler pesticide assessment methodology that relied only on the statistical characterization of precipitation, watershed, and various receiving water body characteristics could be developed to replace the more detailed CMRA Methodology. Computer results of the Four Mile Watershed case obtained by the CMRA Methodology were used for this analysis. Study results indicate that dissolved pesticide concentrations both at stream-edge and instreams can be expressed best by a log-normal distribution among gamma, normal, and log-normal distributions. To develop a statistical relationship among all parameters describing the characteristics of precipitation, watersheds, streams, and pesticides, the computational time required for a large number of simulations may become excessive, however.

Companion reports to this document are _Mathematical Model SERATRA for Sediment and Contaminant Transport in Rivers and Its Application to Pesticide Transport in Four Mile and Wolf Creeks in Iowa_, _User's Manual for the Instream Sediment-Contaminant Transport Model SERATRA_, _User's Manual for EXPLORE-I: A River Basin Water Quality Model (Hydrodynamic Module Only)_, and _Frequency Analysis of Pesticide Concentrations for Risk Assessment (FRANCO Model)_.

This report was submitted in fulfillment of Contract No. 68-03-2613 by Battelle Pacific Northwest Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1978 to January 1980, and work was completed as of January 1980.

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ACKNOWLEDGMENTS

This study was sponsored by the U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA. The authors extend their deepest appreciation to Mr. Robert B. Ambrose at EPA, Athens and Dr. James W. Falco at EPA, Office of Research and Development for their guidance and patience. The authors also wish to thank Dr. John G. Eaton at the U.S. Environmental Protection Agency, Environmental Research Laboratory Duluth, Minnesota for providing much of the toxicological information used in the development of the risk assessment procedure.

SECTION 1

INTRODUCTION

Pesticides have long been recognized to cause a serious nonpoint source pollution problem. The use of chemicals to control pests on agricultural lands has increased dramatically in the last three decades and is still rising. Between 1966 and 1976, pesticide production increased from 450,000 tons to 640,000 tons. More than half of these pesticides were used by agriculture (EPA, 1972).

Many of these pesticides are highly toxic to fish and other aquatic biota. Four major factors are responsible for the detrimental environmental effects which may result from the use of pesticides: 1) some of them are very persistent, so that even very low levels of these pesticides in agricultural runoff may be of environmental concern; 2) they may be both acutely and chronically toxic to fish; 3) pesticides are sometimes widely and indiscriminantly used more as a preventative measure than as a cure in controlling pests; and 4) some pesticides are found to bioconcentrate in aquatic organisms resulting in a potential danger to man through the food chain.

In order to assess the impacts caused by both direct and indirect activities of man, technically sound methodologies are required to predict water quality degradation. Currently, there are no comprehensive methodologies which can be used to evaluate the aquatic impacts which may result from the application of pesticides. Consequently, a definite need exists for the development of such a methodology. To meet this need, this study was conducted to achieve the following objectives:

1) Develop a methodology to predict the occurrence and duration of pesticide concentrations in surface waters receiving runoff from agricultural lands, and

2) Develop a preliminary risk assessment procedure to predict the potential damage to aquatic biota.

In addition to the development of this methodology, the feasilibity of fitting overland and instream pesticide concentrations with statistical distributions was examined. This task was conducted to determine if a simpler statistically based pesticide assessment methodology could be developed to replace the more detailed computer model based methodology.

In this report, Section 2 discusses overall conclusions and recommendations of this study, including the applicability and limitations of the methodology, study results on the feasibility of the simplified statistical methodology, and suggested future studies. Section 3 describes how pesticides applied to agricultural lands behave on watersheds and in receiving streams. This section also briefly discusses physical and chemical characteristics of pesticides. The pesticide assessment methodology is described in detail in Section 4. The methodology was applied to the Four Mile Creek Watershed and to Four Mile and Wolf Creeks in Iowa to demonstrate its feasibility and limitations. Results of this application are discussed in Section 5. An evaluation of the methodology in light of the methodology application is presented in Section 6. Section 7 describes study results on the feasibility of the simplified statistical methodology.

This report also contains the following three appendices: 1) Appendix A, describing the step by step application procedure of the methodology; 2) Appendix B, presenting a grouping of pesticides and their physical, chemical, and toxicological characteristics, and 3) Appendix C, indicating distribution coefficients, Kd, of various pesticides.

Companion reports to this document are Mathematical Model SERATRA for Sediment and Contaminant Transport in Rivers and Its Application to Pesticide Transport in Four Mile and Wolf Creeks in Iowa, User's Manual for the Instream Sediment-Contaminant Transport Model SERATRA, User's Manual for EXPLORE-I: A River Basin Water Quality Model (Hydrodynamic Module Only), and Frequency Analysis of Pesticide Concentrations for Risk Assessment (FRANCO Model).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The Chemical Migration and Risk Assessment (CMRA) methodology was developed for this project and applied to the Four Mile and Wolf Creek area in Iowa to examine its applicability and limitations. The following conclusions were obtained from this study:

1) Application of the CMRA Methodology to the Four Mile Creek watershed and Four Mile and Wolf Creeks in Iowa demonstrates that it is capable of predicting migration and fate of pesticides from agricultural lands and in receiving streams and of assessing pesticide impact on aquatic biota. However, because of the lack of data, the methodology was not fully verified.

2) More specifically, since the methodology uses the state-of-the-art overland and instream models, the Agricultural Runoff Management (ARM) model (Donigien and Crawford 1976), SERATRA (Onishi et al. 1979b) and EXPLORE-I (Baca et al. 1973) to continuously simulate nonpoint source pollution prcoesses of both dissolved and particulate contaminants, it is useful for evaluating both short- and long-term migration and fate of pesticides.

3) Hence the CMRA Methodology can be used as:
   a) a scientific decision making tool for regulation of toxic contaminants including pesticides and toxic substances.
   b) a research tool to estimate relative significance of various transport and degradation phenomena.
   c) a tool to evaluate the effectiveness of various management practices to control toxic chemicals in the environment, and
   d) a means of identifying amounts of gaps and future needs in the risk assessment of contaminants.

4) The CMRA Methodology can be applied to large river basins by segmenting the drainage area into smaller catchments whose sizes are limited by ARM's applicability.

5) The methodology is applicable to nontidal rivers, streams and narrow impoundments. However, because of the limitations of EXPLORE-I, which was used to provide hydrodynamic data to the instream sediment

contaminant transport model, SERATRA, the methodology has limited applicability to very small streams. This limitation may be eliminated by replacing EXPLORE-I with another appropriate hydrodynamic model.

6) The risk assessment procedure, coupled with the statistical analysis of instream pesticide concentrations by a computer program FRANCO and pesticide toxicity data provides a good scientific basis for the pesticide risk assessment. However, due to a lack of extensive knowledge on pesticide toxicity, the risk assessment procedure includes only direct effects of dissolved pesticide concentrations on aquatic biota.

7) Since the CMRA Methodology requires rather extensive field and laboratory data, applicability and accuracy of the methodology could be impaired by the availability of required data.

8) The CMRA Methodology is general enough to be applicable to not only pesticides, but to other hazardous substances and toxic chemicals, as well.

9) Both dissolved and particulate pesticide concentrations at the streamedge and instream were found to be best expressed by log-normal distributions. However, because of the complexity of migration and fate of pesticides on land surface and in stream, the preliminary feasibility study concludes that the development of the simplifed statistical methodology requires an excessive amount of computational time to cover a wide range of variables involved in order to derive general statistical functional relationships among them. Feasibility of the simplified statistical methodology requires further careful examination.

RECOMMENDATIONS

Examination of the applicability and limitations of the CMRA Methodology leads to the following recommendations:

1) While the capabilities of the CMRA Methodology were partially tested using the Four Mile Creek Watershed data, more comprehensive data are required to fully evaluate all aspects of the methodology.

More specific recommendations related to each component of the CMRA Methodology are presented below:

2) The following three considerations are recommended to extend the overland model, ARM:

   a) Modification of ARM will be needed to include the effects of tillage operations on runoff volumes and peaks.

b) Coupling of the ARM and SERATRA models can be improved by modifying ARM to simulate the erosion of different sediment size fractions and by partitioning of the pesticide to each sediment size fraction.

c) Reduction of the data requirements for the overland pesticide modeling component can be achieved by determining how model coefficients obtained during the calibration of ARM on a small catchment change when the model is applied to larger size catchments.

3) Additional improvement and extension of the instream transport modeling can be achieved by conducting the following:

   a) SERATRA should be extended to include hydrodynamic modeling (this will eliminate the use of a separate hydrodynamic code and thus delete the process of transferring hydrodynamic information from EXPLORE-I or other hydrodynamic codes to SERATRA).

   b) Although EXPLORE-I was used for this methodology to supply hydrodynamic information to SERATRA, othr hydrodynamic models can be used to simulate water movements in rivers. If other hydrodynamic models are selected, the compatibility of the hydrodynamic models and SERATRA needs careful attention.

   c) TODAM, a simplified one-dimensional version of SERATRA is recommended to be used for cases where vertical distributions of pesticides are not needed.

   d) It is recommended that this methodology be extended to estuaries and coastal areas where SERATRA is not suited. This can be achieved by replacing current EXPLORE-I/SERATRA models by other models suitable to these environments (Onishi and Wise 1978).

   e) More detailed and basic field and laboratory studies should be conducted to investigate cohesive sediment transport, pesticide adsorption/desorption mechanisms and chemical and biological degradation of pesticides.

4) Additional studies must be performed to assess pesticide toxicity and migration pathways. Specifically:

   a) The effects of low-level intermittent pesticide concentrations on resistance building or cumulative adverse reactions of the organism should be examined.

   b) It is recommended that actual field testing results be correlated with laboratory bioassays.

c) The relationship between toxic effects of dissolved pesticide uptake and the effects arising from ingestion of particulate pesticides should be determined.

d) A more meaningful representation needs to be established regarding the likelihood of adverse effects from concentrations between the LC50 (a median lethal concentration) curve and the MATC (Maximum Acceptable Toxicant Concentration) range. An indicator such as an LC20 would provide more definition to the area greater than the MATC and less than the LC50 curve.

e) Where a high potential for food chain biomagnification exists, it must be identified and be included in the interpretation of risk assessment results.

5) MATC studies and more complete toxicity testing should continue. Future pesticide registration should require fish bioassay data on an extended time interval such as 120 or 168 hours for slower-acting, cumulative, or persistent chemicals.

6) An accessible compendium of up-to-date time-LC50 response data should be available as support for future risk analyses.

SECTION 3

GENERAL REMARKS ON PESTICIDES

Pesticides are used to kill or inhibit the growth of certain undesirable organisms inhabiting a particular region. They may be classified into various categories such as insecticides, herbicides, fungicides, nematicides, and rodenticides, based on a target life form. Each pesticide has different physical, chemical, and biological properties, depending on its chemical structure. Often, compounds of similar structure will behave in a similar manner, thus allowing for the organization of pesticides into general chemical family groups as described in Appendix B. Some of these groups are the organochlorines, organophosphates, carbamates, phenylamides, phenoxyalkanoates, and triazines. Agricultural usage accounts for about one-half of the total pesticide consumption annually. Other major uses include pest control in parks, golf courses and other recreation areas, along highways, utility lines and rivers, and in home lawns and gardens. The focus of this report is limited to pesticides applied to agricultural lands.

Pesticide sprays and dusts are seldom pure formulations of the active chemical compound. Usually a wetting agent, emulsifier, or filler is present. The low water solubility of many pesticides requires some additive to facilitate application. Toxicity of a pesticide may change because of the differences in chemical properties of the additive and the bond of the pure compound with the filler. In some cases an additive may prove more toxic to a species than the active ingredient itself.

Most pesticides are aerially applied by spraying or dusting a target area. Some of the pesticide remains in the atmosphere or is deposited outside the target area during the spraying operation due to pesticide volatility, gaseous drift, and deposition. Deposition of a pesticide outside the target area by rain or particle settling may result in contamination of water sources and increased risk to nontarget species.

After a pesticide has been deposited on the ground, it may be lost to the atmosphere by wind erosion of soil which has adsorbed the pesticide and by vaporization or codistillation of certain pesticides from moist surfaces. The rate of vaporization at the soil-air interface depends on the concentration and properties of the pesticide as well as soil moisture, soil clay and organic content, soil temperature, temperature and relative humidity of the air at the soil level, and the wind speed over soil surfaces.

Pesticides applied to a field exist in either dissolved or particulate form associated with soil particles. Heavy rainfall shortly after pesticide application may result in runoff and soil erosion which physically removes the dissolved and particulate pesticide from the target area. Light intensity rainfall promotes the leaching of nonsorbed pesticides into the soil profile and may dilute the remaining concentration beyond its effective level. It may be possible for the pesticide to enter ground water if the soil texture is very loose and precipitation is sufficient, particularly where the water table is near the ground. However, most pesticide enters into a waterway as a result of surface runoff.

The migration of a pesticide is influenced by the amount and intensity of precipitation or irrigation, temperature and other climatic conditions, pesticide solubility, soil clay and organic content, soil particle size distribution, adsorptive qualities of the pesticide, and watershed characteristics.

The leachability of a pesticide is determined by the soil texture and cation exchange capacity, amount of organic content, amount and intensity of rainfall or irrigation, the mechanical placement of the pesticide, and the adsorptive properties of the pesticide. Insecticides may enter the soil by direct application or by washing off plants. Herbicides are often incorporated into the top few inches of soil for proper performance. Adsorption onto clays and organic materials in the soil may inactivate pesticide movement and render the individual molecules unavailable for solubilization or for plant uptake.

Common ways to express the adsorption/desorption mechanism of pesticide with soil are to use the Freundlich adsorption/desorption isotherm or the distribution coefficient, Kd. The Kd value is the ratio of the amount of the adsorbed pesticide to the unadsorbed dissolved portion. An in-depth discussion of distribution coefficient along with estimated values of Kd for various pesticides in water bodies may be found in Appendix C.

The length of time a pesticide remains effective depends on its persistence. Overall persistence of a pesticide in soil or water is dependent on physical removal as well as biological, chemical, and photochemical degradation. In many cases, a more toxic but less persistent chemical has less environmental impact than a less toxic but more persistent one. For this reason many of the very persistent chemical pesticides are now banned.

Degradation occurs when the complexity of the chemical complex is reduced by splitting the molecule in some way. Primary degradation is the minimum change necessary to alter the chemical's structural identity. Acceptable degradation is the minimum change necessary to remove some undesirable property such as toxicity. Ultimate degradation is the complete breakdown of the organic molecule to water, carbon dioxide, and inorganic elements such as nitrogen and chloride. Biodegradation and in some cases, burning, are probably the only naturally occurring processes capable of ultimate degradation.

Usually the initial degradation step will detoxify a toxic compound. Occasionally the degradation products will also be toxic and could be more deadly than the original formulation such as in the case of aldrin whose degradation product is dieldrin. Toxicological synergism of a compound with its degraded product has been found with malathion and its breakdown product, diethylfumate. Further research may reveal other examples where an increase in toxic effects is related to such synergism.

The pesticide degradation rate in soil depends on soil temperature, moisture, strength of binding by soil surfaces, soil type, meteorological conditions, cover crops, soil cultivation, soil microorganisms, method of application, and pesticide formulation. Oxidation, hydrolysis, and microbial enzyme action are the most common methods of degradation. Photodegradation, the chemical breakdown caused by light, may occur where pesticides have been applied to a moist soil surface for an extended period of time without rainfall. A chemical that breaks down rapidly in moist soils could be very persistent in dry soils. Sometimes persistence is listed in terms of the effective half-life of the compound as a relative indicator of chemical persistence. However, as with other persistence values, the half-life is an estimate based on a particular set of soil and climatic conditions. Persistence may be changed by the amount of pesticide applied and the type of formulation additive.

The rate of biological degradation is dependent on environmental factors and the availability of microorganisms whose enzymatic systems can break down the pesticide molecular structure. For this to be initiated, the compound must reach the microorganism or sometimes, more specifically, the enzyme site, and it must not be lethal to the organism. The organism must have the enzyme system present or be able to induce one necessary for chemical degradation. Without the proper enzymes, the water soluable compounds will probably be excreted, and the insoluable compounds may be stored.

A pesticide entering a waterway arrives either in the dissolved form or particulate form (those adsorbed by sediment) during runoff. What happens to it after that point depends on stream conditions and chemical characteristics. Some pesticides are very soluble and will stay dissolved in the water. Others will remain in suspension or be deposited to the river bottom after being adsorbed by sediment.

Persistence of a pesticide in the surface water depends on its rate of degradation and its rate of removal from the stream. A compound in the water may be broken down by hydrolysis, oxidation, photolysis, or microbial degradation. Persistence is usually greater in static water than in active flowing streams and is influenced by salinity, pH, dissolved oxygen, and amount of organic material present. Pesticide concentration is reduced by flushing downstream, volatilization into the atmosphere, adsorption onto the bank soil and bottom sediment, and plant and animal uptake. Reduction in pesticide concentration by sorption and uptake may be temporary. The scouring velocity of flowing streams may resuspend the sediment, and concentration changes in the dissolved pesticide fraction may favor desorption from suspended or bottom sediment.

Residues in plants and animals may also be recycled back into the stream or transferred to predatory organisms. If the pesticide degrades quickly to a nontoxic species, its metabolites should pose little environmental impact.

The existence of a pesticide in a stream may have a measurable effect on local fish and other organisms. Toxicity may be direct in the form of lethal or sublethal responses. Indirect effects may be exhibited through biomagnification of pesticides through the food chain.

Parameters affecting a pesticide's toxicity to a given species include temperature, turbidity, pH, dissolved oxygen, its concentration, and chemical loading of the streams. These may act synergistically or antagonistically. The chemical properties of the pesticide themselves are of utmost importance as they dictate reaction trends with the various water quality factors. Most of these reactions increase or decrease the fraction of dissolved pesticides to the adsorbed, inactivated fraction. For example, most pesticides are more soluble at higher temperatures. If raising the temperature promotes a greater concentration in the dissolved phase, and thus a higher concentration in contact with fish, toxic effects would be expected to increase. Changes in pH may have a similar effect by changing the relative pesticide-sediment and pesticide-water affinities. The electrolytic loading of a stream will tend to reduce the amount of pesticides that can dissolve in river water. Any reduction in the amount of dissolved oxygen in the water may hamper the organism's efficiency for oxygen uptake and decrease its ability to tolerate other undesirable effects. Suspended solids can cause abrasion to or clogging of the gills, possibly impairing respiration. The dependence of the effect of each of these factors can be somewhat generalized but is actually unique to each pesticide (Guenzi 1974).

Biological aspects also influence pesticide toxicity. The life stage of an organism is a crucial component as pesticides may be harmless to adult members but lethal to embryo and fry. This lethality is due particularly to the method of intake and the metabolic process affected. Metabolic differences between fish strains of the same species may exhibit variability in toxicity as will comparisons of resistant and nonresistant species.

Partially because of the lack of toxicological knowledge of particulate pesticides on aquatic biota, the dissolved pesticide fraction is usually regarded as the main source of toxicant exposure. It enters the organism by crossing membranes of aquatic biota. The effect of the pesticide will depend on its concentration, duration in the water, and its particular toxic properties. Food sources may contribute to ingested pesticide exposure.

Some organisms can adapt to reduce toxic effects. Mobile species may sense the presence of a chemical and seek to avoid it. Others escape harmful effects through genetic resistance. These latter organisms, however, can be particularly hazardous to predator species if the pesticide they resist bioconcentrates to a high degree. Predators may receive a lethal dose from a high concentration in the prey.

As discussed above, the pesticide released to environment undergo complex interactions and it is very difficult to assess its impact on aquatic biota. Mathematical models can be used to integrate many of these complex mechanisms controlling transport and fate of toxic chemicals in the environment into a single framework so that chemical migration, fate, and potential risks can be more accurately evaluated. Hence, the Chemical Migration and Risk Assessment (CMRA) methodology was developed to provide planners and decision makers in government and industry with a sound basis for evaluating the effects of chemical production, use, and disposal.

SECTION 4

CHEMICAL MIGRATION AND RISK ASSESSMENT METHODOLOGY

In this section the Chemical Migration and Risk Assessment (CMRA) Methodology for determination of migration and fate of pesticide and for risk analysis will be discussed. Subsection 4.1 presents an overview of the pesticide risk assessment and its components. In Subsection 4.2, each component of the methodology will be discussed in depth. Step by step instructions to use the methodology are presented in Appendix A.

4.1 GENERAL DESCRIPTION OF THE CMRA METHODOLOGY

The CMRA methodology consists of 1) overland pesticide modeling, 2) instream pesticide modeling, 3) statistical analysis of instream pesticide modeling results, and 4) risk assessment procedure.

Figure 1 provides an overview of the CMRA methodology developed under this study. As shown in this figure, meteorological data, information on pesticide application rates and practices and watershed characteristics are input to the overland pesticide transport model, ARM, to predict runoff, edge-of-stream sediment and pesticide loadings. Using these overland simulation results, hydrodynamic (EXPLORE-I) and sediment-contaminant transport (SERATRA) models predict pesticide distributions in the receiving streams. The simulation results of the in-stream modeling are then used to develop frequency distributions of occurrence and duration of dissolved pesticide concentrations by FRANCO. Finally, the statistical results with pesticide toxicity data are used to assess the acute and chronic impact of pesticides on selected aquatic biota.

Overland Pesticide Modeling

The evaluation of pesticide transport and fate in a receiving water body such as a river requires that the quanity of pesticides contributed to the water body from agricultural lands be determined. Following pesticide application, pesticide losses from agricultural lands can occur through surface runoff, soil erosion, volatilization, degradation (microbial, chemical and photochemical), and uptake by plants and animals. The relative significance of these loss mechanisms is highly dependent on environmental conditions, agricultural management practices, and pesticide properties. Surface runoff and soil erosion have generally been recognized as the dominant mechanisms by which pesticides are moved to a water body.

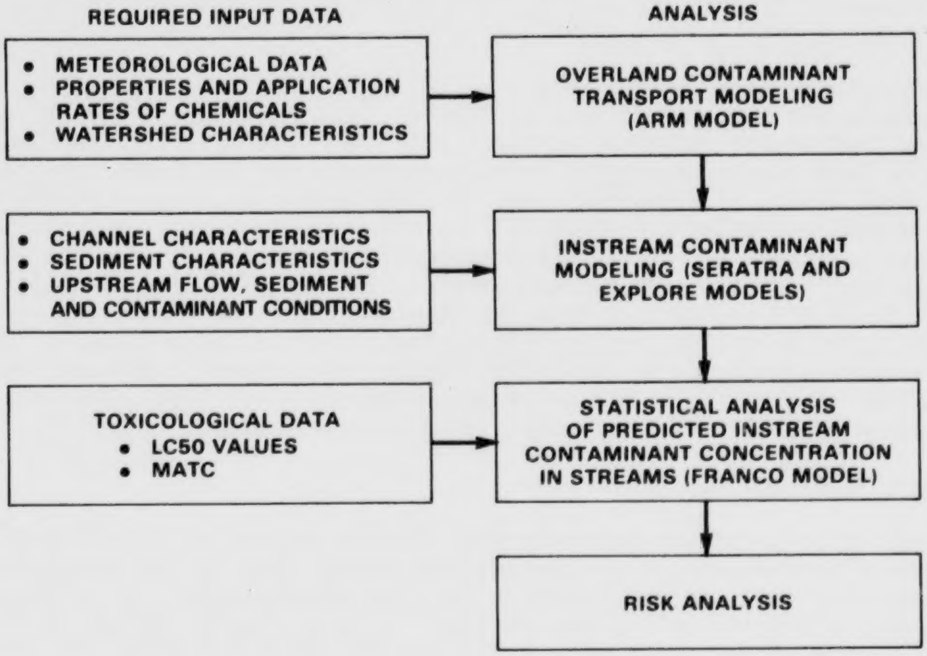

REQUIRED INPUT DATA
ANALYSIS
METEOROLOGICAL DATA
PROPERTIES AND APPLICATION RATES OF CHEMICALS
WATERSHED CHARACTERISTICS
OVERLAND CONTAMINANT TRANSPORT MODELING (ARM MODEL)
CHANNEL CHARACTERISTICS
SEDIMENT CHARACTERISTICS
UPSTREAM FLOW, SEDIMENT AND CONTAMINANT CONDITIONS
INSTREAM CONTAMINANT MODELING (SERATRA AND EXPLORE MODELS)
TOXICOLOGICAL DATA
LC50 VALUES
MATC
STATISTICAL ANALYSIS OF PREDICTED INSTREAM CONTAMINANT CONCENTRATION IN STREAMS (FRANCO MODEL)
RISK ANALYSIS

Figure 1. Chemical Migration and Risk Assessment (CMRA) Methodology

Selecting the most appropriate pesticide loading technique for incorporation into the CMRA Methodology requires an understanding of the types of impacts agricultural chemicals can have on aquatic biota. Pesticides have been found to cause both chronic (or long-term) and acute (or short-term) effects. Organisms which are repeatedly exposed to low levels of pesticides coming off of agricultural lands after storm events can experience chronic effects. Those which inhabit areas along stream channels where contaminated sediments deposit can also experience chronic effects. These effects may range from changes in growth and behavior to the impairment of reproductive activities. Chronic effects are particularly important for highly persistent pesticides like organochlorides. Acute impacts occur most frequently when intense precipitation events take place within several weeks of pesticide application. Under these conditions, runoff pesticide concentrations may vary by an order of magnitude or more during an event (Donigian et al. 1977), and can result in a high rate of mortality. Because both chronic and acute impacts are important, a mathematical model is required to predict both average and peak pesticide concentrations. To accurately predict peak pesticide concentrations, a continuous simulation model is required because of the importance of antecedent conditions in determining the distribution of rainfall between runoff and infiltration during an event. Ellis et al. (1977) recognized the influence of weather sequences in their study of pesticides in the runoff from watersheds in the Great Lakes Basin. A continuous simulation model is also required because the availability of a pesticide for transport by runoff is related not only to the initial loading, but also to previous environmental conditions which affect the degradation and washoff of the pesticide following application.

Therefore, based on the need for detailed, continuous simulation of both short- and long-term pesticide loadings, the Agricultural Runoff Management (ARM) Model (Donigian et al., 1976; 1978) was selected for incorporation into the methodology. ARM was developed for the Environmental Protection Agency by Hydrocomp, Inc. The ARM model is composed of the five major components which simulate: 1) the hydrologic response of the watershed, 2) soil erosion, 3) pesticide adsorption and removal, 4) pesticide degradation, and 5) nutrient transformation and removal. The hydrologic component of ARM was derived from the Stanford Watershed Model; versions of this model have been successfully tested on over 50 watersheds in the United States (Donigian et al. 1977). While the sediment and pesticide components of ARM have only been tested on several watersheds, testing of most other nonurban, nonpoint models is even more limited.

Instream Pesticide Modeling

Pesticides reaching receiving water bodies from agricultural lands migrate in both dissolved and particulate forms. Most of the pesticides adsorbed from solution onto sediment will be concentrated. This process may create a significant pathway to higher trophic levels through the food chain. Sediment contaminated by pesticides may be deposited on the river bed, becoming a long-term source of pollution through desorption and resuspension. In contrast, sorption by sediment can be an important mechanism for reducing the area of influence of these pesticides by decreasing dissolved pesticide concentrations. Other important mechanisms which reduce pesticide concentrations in streams are volatilization, and chemical and biological degradation. Chemical degradation of pesticides occurs through hydrolysis, oxidation, and photolysis.

To obtain accurate temporal and spatial distributions of pesticides in streams, a mathematical model must include all the important mechanisms of both dissolved and particulate pesticide transport phenomena, such as advection, and dispersion of pesticides, interaction of pesticides with sediment, and chemical and biological degradation of pesticides.

Presently there are only a few tested transport models capable of simulating both dissolved and particulate contaminants with sediment-contaminant interaction (ORNL 1978; Onishi 1979a). Because one of the most extensively tested models is an unsteady, two-dimensional (longitudinal and vertical) sediment-contaminant transport model, SERATRA (Onishi et al. 1976; Onishi 1977a; Onishi 1977b; Onishi et al, 1979b), this model was selected for the study. The model consists of the following three submodels coupled to include sediment-contaminant interaction: 1) a sediment transport submodel, 2) a dissolved contaminant transport submodel, and 3) particulate contaminant transport submodel. The original SERATRA was modified to include the mechanisms of contaminant volatilization, and chemical and biological degradation caused by hydrolysis, oxidation, photolysis and biological activities. The model calculates changes in the conditions of both river bed sediments and deposited contaminants.

Because both SERATRA and EXPLORE-I use a constant width along each computational cell, the hydrodynamic modeling portion of the one-dimensional general water quality model, EXPLORE-I (Baca et al., 1973), was selected to provide discharge and depth data to SERATRA. However, other dynamic models (e.g., Fread 1973) could be used. The EXPLORE-I code is applicable to rivers, estuaries, and oceans to compute depth and velocity distributions. Although EXPLORE-I itself is one-dimensional, it can calculate the longitudinal and lateral distributions by dividing the simulation area with linked channels. EXPLORE-I has difficulties handling very shallow streams with steep hydrographs.

Computed results from SERATRA are statistically analyzed to obtain the probability of occurrence and duration of given pesticide concentrations. The current knowledge on the toxicity of pesticides has not advanced enough to fully utilize the detailed two-dimensional (longitudinal and vertical) distributions of both dissolved and particulate pesticide concentrations computed by SERATRA for the pesticide risk assessment. Hence only cross-sectionally averaged dissolved pesticide concentrations were statistically analyzed for the risk assessment. However, additional pesticide toxicological data in the future may enable SERATRA model outputs to be more fully used.

Statistical Analysis

A new statistical analysis procedure was developed to provide meaningful summaries of instream dissolved pesticide concentrations for the methodology. The computer program is called FRANCO (FRequency ANalysis of COncentration program).

The statistical characterization of the outputs from SERATRA was designed to provide risk assessment information on the frequency and duration of specified dissolved pesticide concentrations at selected instream locations. The outputs to be summarized are time series of dissolved pesticide concentrations. The procedure horizonally slices the concentration versus time plot at a specified concentration level, counts the number of peaks (or excursions) above the line, counts the amount of time spent above the line, and tabulates the peaks according to their duration. This process is repeated for a range of concentration values. This is the computational basis used to determine the frequency and duration of specific pesticide concentrations.

A concept of global exceedance of an LC-function (i.e., lethal concentration) was also developed for the risk assessment procedure. Laboratory studies on fish provide basic information on the concentration of a pesticide required to kill fifty percent of the population when exposure durations are 24, 48, 96 hours, etc. This information may be used to define a function between concentration and duration such that if a point is above the concentration-duration curve at least fifty percent of the population is killed. These LC-functions are used to summarize both the number of distinct events (i.e., peaks) and the amount of time spent above the curve during the total simulation time. This procedure was developed to eliminate possible double counting of concentration episodes that would result in lethality.

The method used by FRANCO is one possible choice of bridging the gap between simulation results and risk assessment procedures. Similar procedures can be defined having the basic concepts used by FRANCO.

Risk Assessment

This assessment is limited to the direct effects of dissolved pesticides. Ingestion as a second route for toxic effects is not addressed nor are indirect effects such as bioconcentration and biomagnification.

Toxicological assessment of damage to aquatic life is divided into considerations of lethality and sublethal effects resulting from acute and chronic exposures. Acute lethality usually occurs within the first 96 hours (Sprague 1969), whereas effects after 96 hours are often considered chronic. However, the actual dividing time between the two is rather arbitrary.

Important components of the risk assessment procedure include the use of the median lethal concentration (LC50) data for predicting lethality, and the use of chronic data, maximum acceptable toxicant concentration (MATC) values, and application factors for estimating sublethal toxicity. These values can be used in conjunction with the mathematical models to compute the extent of pesticide contamination in a stream and the resulting probabilities of lethal or sublethal effects.

The importance of lethality expressed as LC50, or the median tolerance limit (TLm) is paramount to the assessment process. For lack of more adequate data, these values are applied to estimate the likelihood of fish kills due to particular toxicant concentrations and durations at lethal levels. The results are expressed as a probability. Use of the LC50 is justified by its common and historical usage as a parameter of toxicity. The LC50 is a more reliable indicator than LC5 or LC100, for example, because the variability of the average toxic range is usually quite narrow, while the distribution of fish kills at the extremes tends to be much more variable. Use of the LC50 does, however, limit predictions of fish kills to median lethality rather than threshold lethality for any single member of the population.

Chronic toxicity is usually recorded as the amount of toxicant causing measurable effects. These effects are typically described by symptoms. Effects resulting in a decrease in growth, maturation, or survival of the individuals, an increase in physical deformities, a decrease in reproductive ability demonstrated by a decrease in the number of eggs, and the reduced hatchability of the offspring are the criteria most often used to assess chronic toxic effects. Results from such bioassays are either descriptive, associating a given effect with a particular concentration, or they are cited in terms of MATC range for the chemical. The lower value in the MATC range is the highest concentration tested which produced no defined adverse effects. The higher range value is the lowest tested concentration which resulted in a chronic effect.

Sublethal effects may result from concentrations greater than the MATC range if exposure time is sufficient. Chronic bioassays are useful as indicators of the minimum amount of toxin producing certain deleterious effects on the organism.

The amount of toxicant required to produce a sublethal effect differs with the amount of exposure time. For example, a species may show no effects from a ten-day exposure to a chemical but may sustain damage when exposed for 30 days at the same concentration level. The species may also suffer reproductive impairment at some future point.

The mathematical model requires the input of a sublethal indicator for prediction purposes. MATC values are based on long-term tests which may overestimate toxicity when applied to shorter time frames. However, unless the researcher has access to chronic data for all time steps under evaluation, use of the MATC values as a sublethal boundary indicator is the best alternative available.

While long-term toxicity testing and the use of MATC values are becoming more common, many pesticides have not yet been tested for this parameter. Those for which MATC data is available focus on a small number of species because of the complexities of life cycle testing. Where MATC values are not available, they may be estimated by the use of an application value which can be calculated or assigned arbitrarily. The statistically significant mathematical relationship that appears to exist between most LC50 values and MATC ranges is the basis for the use of application factors which can be used to calculate MATC ranges for other species.

LC50 and MATC values are used to estimate various lethality and sublethality curves. These curves are used as input to the statistical analysis code FRANCO. The in-stream migration model (SERATRA) output is evaluated for concentrations exceeding the curves. Global exceedance or lack of concentration-duration periods exceeding the curves forms the basis for interpretation of the hazards from the particular pesticide to the organisms under evaluation. However, risk assessment output from FRANCO must be carefully reassessed by taking into account all other known information on the pesticide characteristics, life stage of the species of concern, possible avoidance, reactions to the pesticide and other pertinent data.

4.2 DETAILED DESCRIPTION OF CHEMICAL MIGRATION AND RISK ASSESSMENT METHODOLOGY

Overland Pesticide Modeling

Various techniques are available for estimating the migration of pesticides from agricultural lands. A relatively simple technique based on loading functions was developed by McElroy et al. (1976). This technique involves the use of the Universal Soil Loss Equation to estimate the average soil loss from a catchment or watershed. Since nutrients, organic matter, pathogens and pesticides are commonly adsorbed to eroded soil materials, pollutant loadings can be estimated by multiplying sediment yields by factors which denote the concentrations of these substances in the soil and the effect of enrichment during the erosion process. In general, the approach is best suited to the prediction of annual average pollutant loads expected to occur over many years.

On the other end of the spectrum of pesticide loading techniques, there are a series of mathematical models which simulate the complex processes affecting pesticide cycling in the environment. Examples of these pesticide transport and runoff models include the Agricultural Runoff Management Model, ARM (Donigian and Crawford 1976; Crawford and Donigian 1973); the Agricultural Chemical Transport Model, ACTMO (Frere et al. 1976); the Agricultural Watershed Runoff Model, AGRUN (Roesner et al. 1976); and the Simulation of Contaminant Reactions and Movement Model, SCRAM (Adams and Kurlsa 1976). Mathematical models such as these are generally capable of simulating: 1) the complex hydrologic processes which act to convert precipitation to runoff, 2) the erosion of soil materials due to rainfall impact and runoff, 3) the partitioning of pesticides between dissolved and particulate (i.e., pesticides adsorbed to sediment) phases, and 4) the loss of pesticide from the soil through volatilization and degradation.

Pesticide transport and runoff models are generally of two types: single-event simulation models or continuous simulation models. In single-event models, the above processes are simulated only throughout the duration of a runoff producing event. Continuous simulation models, on the other hand, not only simulate these processes during an event but also take into account the processes which act to change soil moisture and soil pesticide conditions in-between storm events. As a result, it is not necessary to estimate antecedent conditions prior to the modeling of runoff, sediment and pesticide contributions.

The pesticide loading model selected for incorporation into the CMRA Methodology is the Agricultural Runoff Management (ARM) Model. The basic philosophy of ARM is that the processes controlling runoff, soil erosion and pesticide transport on the land surface are continuous in nature. The status of antecedent soil moisture, land surface, and pollutant conditions are updated continuously even though nonpoint source pollution takes place only during runoff-producing storm events. As a result, the ARM model uses a continuous simulation approach.

The basic hydrologic component of the ARM model was derived from the Stanford Watershed Model (SWM) (Crawford and Linsley 1966). The algorithms used in SWM and the modifications which have been made to it throughout the development of ARM have been reported by Donigian and Crawford (Donigian and Crawford 1976; Donigian et al 1977). Basically, the hydrologic component of ARM simulates the dominant physical processes which act to convert precipitation into runoff (i.e., interception, infiltration, interflow, percolation and evapotranspiration). ARM also has the capability to simulate the mechanisms of snow accumulation on the land surface and runoff due to melting of the snow pack. The transfers of water between the major components of the hydrologic cycle simulated by ARM are not only used to calculate runoff, but are also used in the calculation of soil erosion and the vertical movement of pesticides in the soil profile.

The soil erosion component of ARM simulates sediment loss from the land surface due to both sheet and rill erosion. Soil fines are scoured from the land surface and transported by overland flow. The availability of these materials for transport is a function of rainfall impact. The availability of soil fines is also a function of the tillage operations or conservation practices which have occurred on a watershed.

Pesticides placed in a water-sediment mixture will eventually come to equilibrium, with a certain fraction of the pesticide adsorbed to the sediment materials and the remainder dissolved. The adsorption and removal component of ARM uses a modified Freundlich adsorption/desorption isotherm algorithm to partition the available pesticide between that dissolved in the overland flow and that attached to soil fines being transported by the flow. Both single-valued and non-single-valued formulations of this equilibrium type algorithm have been included in ARM; these formulations are discussed in detail by Donigian and Crawford (Donigian et al. 1977).

The pesticide degradation component of ARM determines the quantity of pesticide available for transport, either by overland flow or by soil erosion, at any time after its application to a watershed. The major processes which act to attenuate pesticides in the soil are volatilization and microbial, chemical and photochemical degradation. These processes, along with plant uptake, remove most of the total pesticide applied to a soil, with runoff and erosion removing only a small fraction. In his review of the literature on the pesticide content of overland flows, Wauchope found that they generally contained less than 0.5 percent of the total applied pesticide (Wauchope 1978). Because reliable models have not been developed for each of these attenuation processes, they are currently grouped together in a simple first order decay algorithm in ARM.

At the initiation of this study, the second version of the ARM (ARM-II) was just being released. As a result, the first version was incorporated into the CMRA Methodology. However, since the mathematical models used in the methodology are only input/output linked, ARM-II can also be used. The only major differences between the models are that in ARM-II: 1) the evapotranspiration index parameters can vary on a monthly basis, 2) a soil compaction factor has been added to represent the natural aggregation and mutual attraction of soil particles and the compaction of the surface soil zone, 3) different first-order pesticide degradation rates can be assigned to specific time periods after pesticide application, and 4) chemical leaching factors have been added so that the amount of pesticide moving with infiltrated or percolated water can be changed. These differences are described in detail by Donigian et al. (1977) and Donigian and Davis (1978).

The use of both versions of the ARM model is described in detail by Donigian and Davis (1978). The major steps which are followed in the application of ARM include: 1) data collection and analysis, 2) preparation of meteorologic data and model input sequence, 3) parameter evaluation, 4) model calibration and verification, and 5) production of needed information and analysis of simulation results. The first three steps basically involve the compilation and analysis of hydrologic and meteorologic data and information on the watershed soil characteristics, topography, cropping patterns and pesticide usage. Specific data requirements and data sources are also reviewed by Donigian and Davis (1978). The fourth step involves the calibration or adjustment of model parameters to improve agreement between simulated and recorded information. This process ideally requires that detailed data be available on runoff, erosion and pesticide contributions from the study area for at least three years in order to accurately evaluate model coefficients. The final step involves the application of ARM to the selected study area.

One of the key limitations of the model is the amount of comparative data required to calibrate model coefficients. In order to test the CMRA Methodology developed in this study, numerous agencies were contacted in an attempt to locate a comprehensive set of data. It was found that relatively few complete sets of data are available and that most of the available data had been used in the testing and development of ARM-I and ARM-II. This limitation has been reduced somewhat by the regionalization of many of the hydrologic parameters. The hydrologic component has been applied to over 50 watersheds throughout the United States (Donigian et al. 1977). The data limitation has also been reduced by the use of pesticide adsorption/desorption and degradation algorithms with parameters that can be estimated through laboratory and field studies; many of these parameters can be found in the open literature or obtained from pesticide manufacturers. Additional testing and application of sediment and pesticide algorithms may also serve to reduce the model's data limitations.

A second limitation is that the ARM model is not formulated to handle the effects of channel processes on runoff and sediment transport. As a result, the model is applicable only to watersheds that are small enough that channel processes can be assumed negligible. While the limiting size varies with climatic and topographic characteristics, it was found to be approximately 2 to 5 km^2 (or about 1 to 2 mi^2) (Donigian and Crawford 1976). Because of this limitation, an application of ARM to a large watershed requires a number of individual model applications to smaller subcatchments.

The overland modeling component is the first step in the CMRA Methodology. Based on known or selected tillage practices and pesticide application rates, ARM is applied to the study area to obtain a continuous history of runoff and edge-of-stream sediment and pesticide loadings. This information is then used as input to the second step of the methodology, in-stream pesticide modeling.

The length of the study period is primarily based on the availability of meteorological data, the projected computation time for the methodology and the desired representativeness and stability of the statistical summary of instream pesticide concentrations.

Instream Pesticide Modeling

A number of general water quality models (Baca et al. 1973; Norton et al. 1970; Leendertse 1970) could be used to simulate pesticide migration, but none of them includes the mechanisms of adsorption of pesticides to sediment, desorption from sediment, and transport, deposition and resuspension of particulate pesticides associated with sediment. Computer simulation models which calculate pesticide transport without including the pesticide-sediment interaction predict that pesticides will be flushed from surface waters at the same rate at which water is exchanged. In reality, however, sediment sorption effects cause some pesticides to flush much more slowly, e.g., at the approximate rate at which the sediment is exchanged in the surface water system (EPA 1978). Hence, in some cases, neglecting these sediment effects prohibits accurate prediction of pesticide migration (Onishi and Wise 1978).

In order to include sediment-pesticide interactions for the instream pesticide modeling, the sediment-contaminant transport model, SERATRA, was selected for this study. The hydrodynamic modeling portion of EXPLORE-I is used to provide discharge and depth data to SERATRA. Input data for EXPLORE-I are channel geometry and Manning's roughness coefficient, together with initial and boundary flow conditions. Outputs of EXPLORE-I are unsteady, cross-sectionally averaged distributions of velocity (or discharge) and depth. Using the cross-sectionally averaged results provided by EXPLORE-I, SERATRA distributes a velocity vertically by assuming either a logarithmic velocity distribution or a uniform distribution. A description of the EXPLORE-I model formulation and user's manual were prepared by Baca et al. (1973) and Onishi (1979e). Although EXPLORE-I was used for this study, other compatible hydrodynamic-water quality models such as QUAL-II (Norton et al. 1970) may also be used to provide hydrodynamic data to SERATRA.

SERATRA is an unsteady, two-dimensional (longitudinal and vertical), sediment-contaminant transport model which utilizes the finite element computation method with the Galerkin weighted residual technique (Onishi et al. 1976; Onishi et al. 1979b)). The model uses the general convection-diffusion equations with appropriate boundary conditions. It consists of three submodels coupled to include the effects of sediment-contaminant interaction. The submodels are: 1) a sediment transport submodel, 2) a dissolved contaminant transport model, and 3) a particulate contaminant transport submodel. A detailed description of the SERATRA model formulation and a user's manual were prepared by Onishi and Wise (1979c; 1979d).

Sediment transport submodel: The sediment transport submodel solves the migration (transport, deposition and scouring) of cohesive and noncohesive sediments. The migration of three sediment size fractions can be modeled since the movements and adsorption capacities of sediments vary significantly with sediment sizes. The submodel includes mechanisms of:

1. Convection and dispersion of cohesive and non-cohesive sediment,
2. Fall velocity and cohesiveness,
3. Deposition on the river bed,
4. Resuspension from the river bed (simulating bed erosion and armoring), and
5. Sediment contributions from tributaries (contributions from overland runoff and other sources may be treated as a part of the tributary contributions).

This submodel also calculates river bed conditions, including changes in river bed elevation and the distribution of each sediment component within the river bed.

Dissolved and particulate contaminant transport submodel: Both the dissolved and particulate contaminant transport submodels include mechanisms of:

1. Convection and dispersion of dissolved and particulate contaminants,
2. Adsorption (uptake) of dissolved contaminants by both suspended sediment and bed sediment, or desorption from sediments into the water,
3. Chemical and biological decay and degradation resulting from hydrolysis, oxidation, photolysis, and radionuclide decay where applicable,
4. volatilization
5. Deposition of particulate contaminants on the river bed or resuspension from the river bed, and
6. Contaminant contributions from tributaries and other sources (contributions from overland runoff, wastewater discharges, fall out and groundwater are treated as a part of the tributary contributions).

Effects of water quality (e.g., pH, water temperature, and salinity) and sediment characteristics (e.g., clay minerals, and organic content) can be taken into account by changing distribution coefficients (which partition the contaminants between particulate and dissolved forms) and contaminant transfer rates to reach equilibrium conditions assigned by distribution coefficients. Transport of contaminants which are attached to sediments is solved separately for those adsorbed by each sediment size fraction. The contaminant distribution within the river bed is also computed.

SERATRA is applicable to rivers and impoundments. Since SERATRA uses a marching solution technique along a longitudinal direction, a reverse flow condition (such as tidal flows) cannot be handled. One of the advantages of SERATRA is that it can be applied to water bodies over large longitudinal distances and shallow depths. SERATRA has been applied to a wide range of hydraulic conditions, including the large, heavily regulated Columbia River (Washington) (Onishi et al. 1979b) and the intermediate size Clinch River (Tennessee) (Onishi 1977a). Application of SERATRA to swift streams such as Cattaraugus and Buttermilk Creeks (New York) is currently underway.

Statistical Analysis

The usefulness of the simulated instream pesticide concentrations depends in part on how they are statistically summarized for risk assessment. The statistical analysis bridges the gap between SERATRA output and the risk assessment procedure. The risk assessment procedure estimates the probability of lethality or sublethality affecting a given species from aquatic exposure to a particular pesticide. SERATRA provides a continuous prediction of cross-sectionally averaged dissolved pesticide concentrations at selected river segment locations. These two parts of the methodology are linked by the statistical summarization computer program FRANCO. FRANCO (FRequency ANalysis of COncentration) and its summary methods were developed especially for this methodology. A detailed description of FRANCO and a user's manual was given by Olsen and Wise (1979).

Statistically summarizing the simulated pesticide concentrations requires a precise interpretation of the phase "frequency of occurrence and duration of pesticide concentrations." The risk assessment procedure provides information on pesticide concentration that will result in an effect if the concentration remains at or above a specified level for a certain length of time. This concept forms the basis for the statistical summary. The summary of the simulated concentrations uses specific definitions for these terms: event and duration of an event. An event defined by a concentration of C occurs when a sequence of simulated concentrations begins below C at time step t_1, becomes and remains greater than or equal to C in subsequent time steps and then drops below C after time step t_2 (see Figure 2 where C is C_5). This is referred to as an event defined by concentration C. The duration of an event defined by concentration C is the length of time from the beginning to the end of the event, e.g., $t_2 - t_1$.

Utilizing preceding concepts of an event FRANCO provides three types of summaries: counts of time steps, counts of events and LC-function global exceedance. The later is defined subsequently. Let $C_1 \; C_2 \cdots C_m$ be a set of concentration levels used to define events. These are based on lethal concentration information from the risk assessment procedure and the concentration range expected from the SERATRA simulation. Let $d_1 \; d_2 \cdots d_n$ be a set of durations selected on the same basis as the concentrations. All of the statistical summaries are completed for events defined by concentrations $C_i (i = 1,2,...m)$ with durations of d_j (j = 1,2,...n,) or greater. Each of the m concentration levels selected conceptually slices the SERATRA concentration time history plot horizontally. A number of concentration peaks occur above the horizontal line. FRANCO counts the peaks (events), counts the time above the line and computes summary statistics based on these counts. Additional detail is provided by completing the above only for events lasting a duration d_j or greater.

The first summary is a count of the number of events defined by concentration C_i with a duration of d_j or greater. This is denoted as $NE(C_i,d_j)$. Events defined by concentration C_i of any duration, i.e., greater than or equal to one time step, are denoted by $NE(C \geq C_i)$. This is equivalent to $NE(C_i,d_1)$.

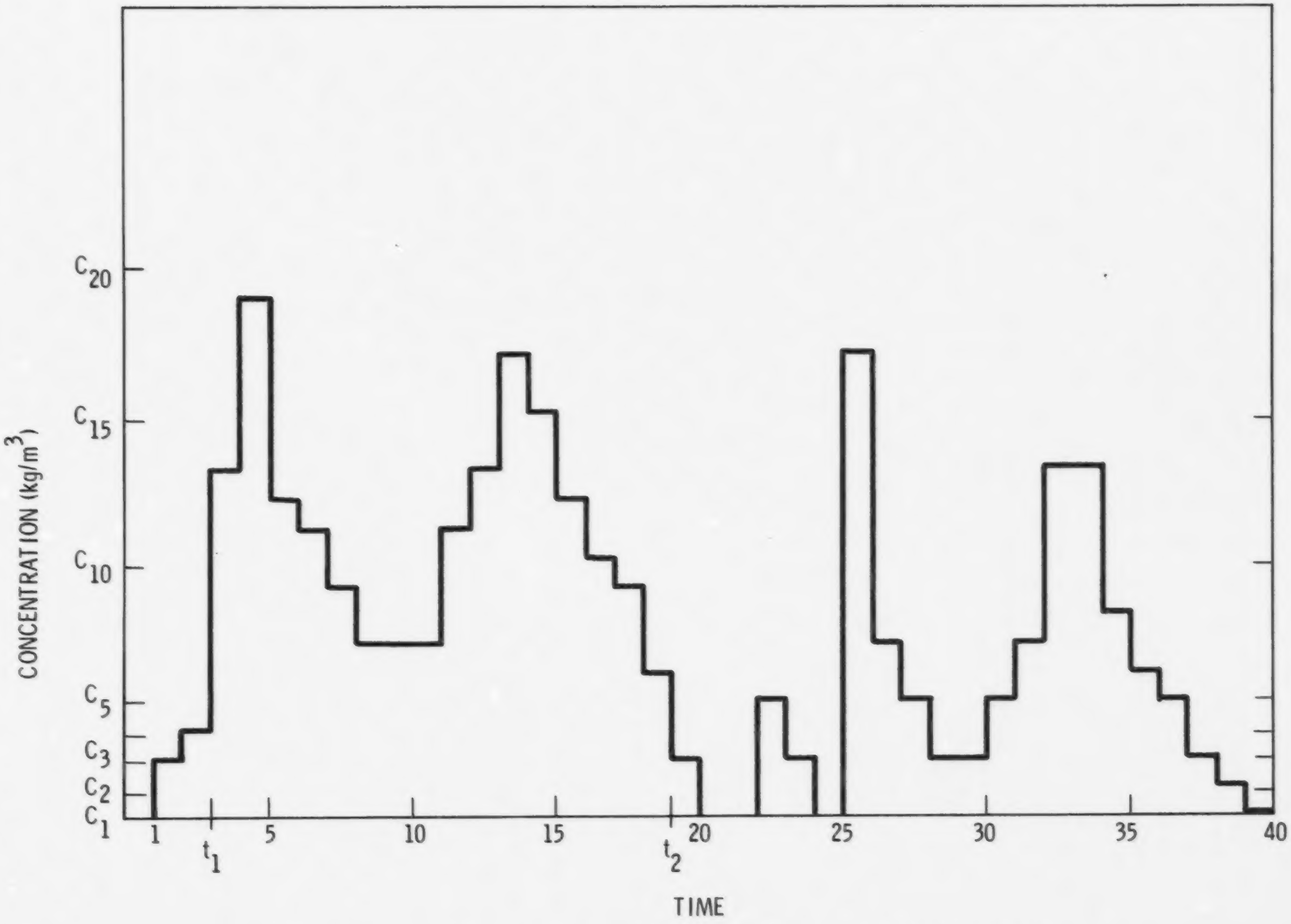


Figure 2. Example of a discrete time step series of pesticide concentrations

The second summary is a count of the number of time steps in all events defined by concentration C_i with a duration of d_j or greater. This is denoted as $NT(C_i, d_j)$. Also $NT(C \geq C_i)$ is equivalent to $NT(C_i, d_1)$.

The third summary measures the frequency of occurrence of concentrations greater than or equal to C_i for all durations. Mathematically, this is given by the fraction:

$$P_T\ (C \geq C_i) = \frac{NT(C \geq C_i)}{T},\ i = 1, \ldots, m$$

where T is the total simulation time and Δ is the time in a single time step. $P_T\ (C \geq C_i)$ is a decreasing function of C_i with $P_{TT}(C \geq 0) = 1$ and $P_T(C \geq C_{max}) = 0$ where C_{max} is the maximum simulated concentration.

As an illustration of these summaries' measures, a particular time series may indicate that for 10% of the time, the concentration is greater than or equal to C_i, i.e., $P_T(C \geq C_i) = 0.10$. At the same time the total number of events that occurred during the fraction of the time may be 5, i.e., $NE(C \geq C_i) = 5$. For another case a single event may be responsible for the 10% figure, i.e., $P_T(C \geq C_i) = 0.10$ and $NE(C \geq C_i) = 1$.

The fourth summary gives frequency of occurrence information for events categorized by duration. It is a generalization of the previous summary and is defined as:

$$P_T\left[C \geq C_i,\ D \geq d_j\right] = \frac{\Delta NT(C_i, d_j)}{T}\ .$$

This gives the fraction of the total time there were events defined by concentration C_i that extended for durations of d_j or greater.

The following two relative frequency summaries resemble conditional probability statements and are useful when additional duration information regarding events defined by concentration C_i is of interest. That is why only one concentration level C_i is to be considered. The summaries are:

$$P_E\left[D \geq d_j \mid C \geq C_i\right] = \frac{NE(C_i,\ d_j)}{NE(C_i \geq C\ )} \quad \text{and}$$

$$P_T\left[D \geq d_j \mid C \geq C_i\right] = \frac{NT(C_i,\ d_j)}{NT(c \geq_i C\ )}\quad .$$

They measure relative frequency with respect to the number of events defined by concentration C_i and the amount of time in events defined by concentration C_i respectively. Laboratory toxicity experiments provide the main basis for developing a risk analysis for fish. A common method of summarizing the results of these experiments is to use a lethal concentration where 50% of the fish die. A concentration, say C^{96}, is determined such that 50% of the fish die when exposed continuously for a specified duration of 96 hr, say d^{96}. The previous summaries give:

a) $NE(C_i, d_j)$; the number of events having durations and concentrations that exceed d_j and C_i, respectively
b) $P_T(D > d_j, C > C_i)$; the fraction of the total time period that the calculated concentration is greater than or equal to C_i for a duration of d_j or greater.

Usually information for LC50 concentrations at 24, 48 and 96 hours is available. This information may be combined in the form of an LC50 curve. In this study it is assumed that an LC curve is represented by up to five peice-wise straight lines, as shown in Figure 3. The summary $NE(C^{96}, d^{96})$ is a count of the number of events in the concentration time series that meet or exceed the 96-hr LC50 value (shaded region above the LC50 curve in Figure 3). This is termed a point exceedance of the LC50 curve. Multiple point exceedances can be measured by judicious choices of d_j and C_i. $[P_T\ D \geq d^{96}, C \geq C^{96}]$ gives the fraction of the total time that the time-series is in the 96-hr point exceedance.

A more comprehensive measure of exceedance is to obtain the fraction of the total simulation time that the calculated pesticide concentration exceeds an LC50 curve (shaded region above the LC50 curve in Figure 4). This is termed global exceedance of the LC50 curve. It is defined as:

$$P_G(\text{LC50}) = \frac{\left[\begin{array}{c}\text{number of time steps in distinct events such that}\\ (C_i\ d_j) \text{ is above the LC50 curve}\end{array}\right]\Delta}{T}$$

This summarization can be conducted not only for an LC50 curve but for other LC curves such as LC90, LC10, etc. An example of the use of this summarization involves deciding whether fish will be killed by acute toxicity or chronic toxicity under a certain condition. Assume that the chronic toxicity has a duration of 96 hour or more. In order to obtain the answer, summarization will be conducted for the following cases: a) Case A has a LC50 curve shown by the solid line in Figure 4, and b) as shown in Figure 5, Case B has a LC50 curve which is the same as the LC50 in Case A for the duration of 96 hour or more but is parallel to the vertical axis at d = 96. P_G for Case A provides the fraction of the total time that 50% of fish will be killed by both acute and chronic toxicity of the pesticide. P_G for Case B provides the fraction of the total time that 50% of fish will be killed by only chronic toxicity. The difference between the values of P_G for Cases A and B will then supply the fraction of total time fish will be killed by acute toxicity.

The remainder of this subsection gives a detailed example of the statistical summaries just described. No new information is given. However, the step by step description is useful in clarifying the concepts of point and global exceedance. The description is given in the order that the

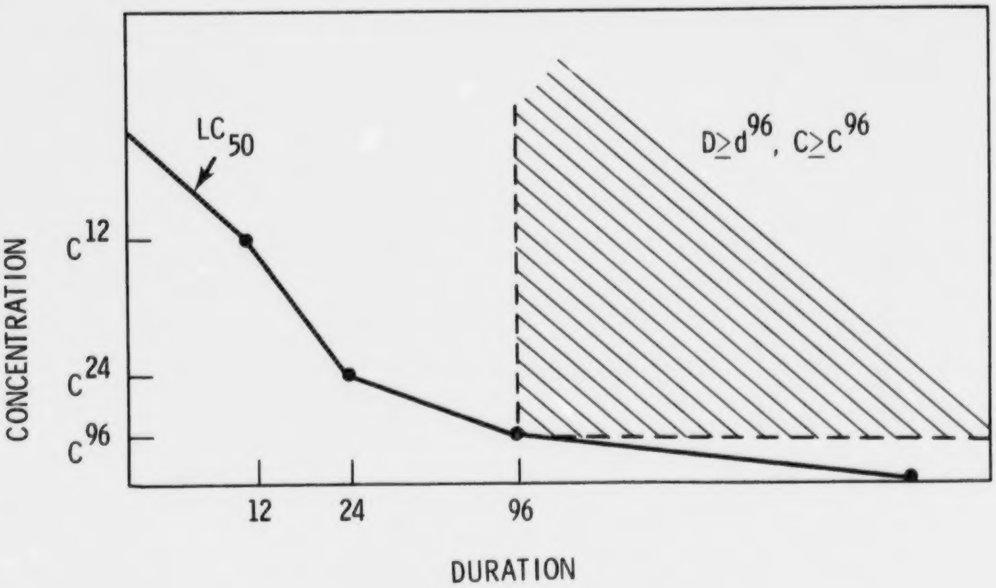


Figure 3. Example of LC50 curve with point exceedance region

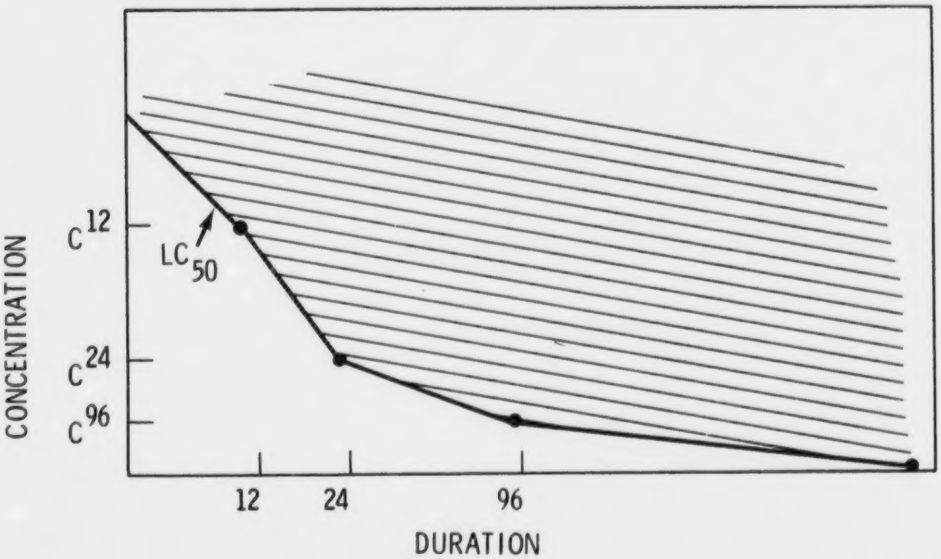


Figure 4. Example of LC50 curve with global exceedance region

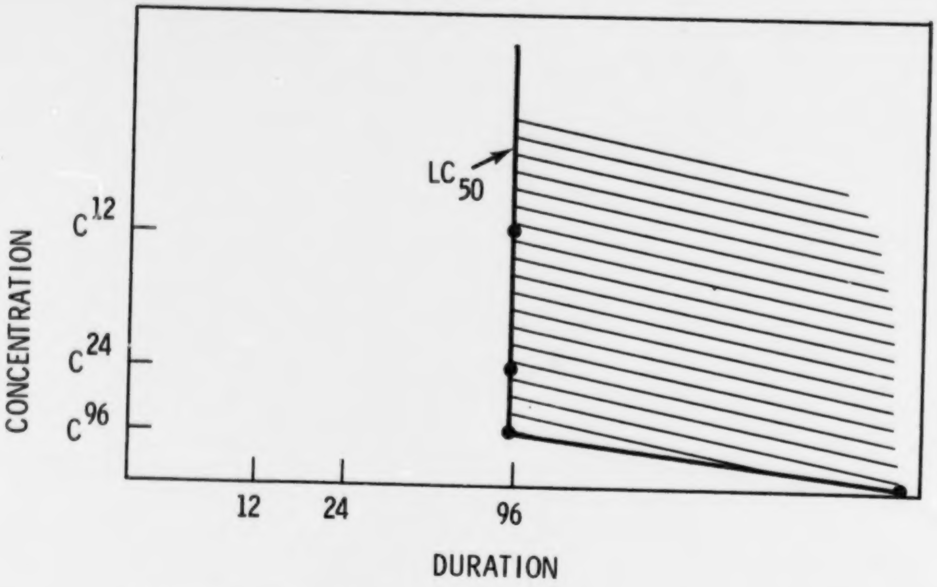


Figure 5. Postulated chronic toxicity global exceedance region

computer program FRANCO completes the analysis. The program documentation and user's manual for FRANCO are available in Olsen and Wise (1979).

As an example, suppose C_1, C_2, C_4, C_{10}, C_{15}, and C_{20} are the specified concentrations and d_1, d_5, d_{10}, d_{15}, and d_{20} are the specified durations. Table 1 presents the number of events defined by concentration levels C_i and duration d_j for the data given in Figure 2. Table 2 presents the number of time steps occurring for all events defined by concentration levels C_i and durations d_j. In the example d_1 was selected to be one time step, C_1 to be zero, and C_2 to be a model output cutoff value above which calculated instream dissolved pesticide concentrations are statistically analyzed. The cutoff value was introduced to FRANCO due to accuracy limitation of the simulation model, SERATRA. Under these restrictions the total number of time steps in the study period is given by $NT(C_1,d_1)$, the number of time steps with simulated concentrations above the model cutoff by $NT(C_2,d_1)$ and the number of events defined by concentrations above the model cutoff by $NE(C_2,d_1)$.

In addition to the tabular summaries of numbers of events and time steps, a compilation of each individual event defined by the input concentrations C_i is kept internally in FRANCO. This compilation, in the order that it is actually completed, is presented in Table 3 to clarify subsequent concepts. Event concentration refers to the concentration level that defines the event.

The statistical summaries available from FRANCO are discussed as they relate to issues of interest in considering the results of a pesticide

TABLE 1. NUMBER OF EVENTS DEFINED BY CONCENTRATIONS C_i WITH DURATIONS OF d_j OR GREATER FOR DATA IN FIGURE 2.

	Duration				
	d_1	d_5	d_{10}	d_{15}	d_{20}
C_1	1	1	1	1	1
C_2	3	2	2	1	0
C_4	4	2	1	1	0
C_{10}	4	1	0	0	0
C_{15}	3	0	0	0	0
C_{20}	0	0	0	0	0

TABLE 2. NUMBER OF TIME STEPS FOR EVENTS DEFINED BY CONCENTRATIONS C_i WITH DURATIONS OF d_j OR GREATER FOR DATA IN FIGURE 2.

	Duration				
	d_1	d_5	d_{10}	d_{15}	d_{20}
C_1	40	40	40	40	40
C_2	35	33	33	19	0
C_4	28	24	17	17	0
C_{10}	13	6	0	0	0
C_{15}	4	0	0	0	0
C_{20}	0	0	0	0	0

simulation project. A cutoff point is used in the SERATRA model below which the simulated concentrations are assumed to be zero. The number of distinct events occurring with concentrations above the model cutoff value is given NE (C_2, d_1). There are three such events in the example. The time over the study period during these events was 35 time steps. Note that if the time steps are in terms of hours, this corresponds to 35 hours. This information is also given as the percent of the total time events defined by C_2 were present.

More specific information is obtained by considering the duration of the events. For example, if a 10 hour LC50 value is given by C_4, then FRANCO gives the number of times this occurred, the total time during these occurrences, and the percent of time during the study period this LC50 condition was exceeded. The number of events is given by NE (C_4, d_{10}), and the number of time steps in events defined by C_4 and d_{10} by NT (C_4, d_{10}),

TABLE 3. COMPILATION OF EVENTS IN ORDER OF OCCURRENCE FOR EXAMPLE DATA

Ending Time Step	Number of Time Steps	Event Concentration
5	1	C_{15}
7	4	C_{10}
15	2	C_{15}
17	6	C_{10}
19	17	C_4
20	19	C_2
23	1	C_4
24	2	C_2
26	1	C_{15}
26	1	C_{10}
28	3	C_4
34	2	C_{10}
37	7	C_4
39	14	C_2
40	40	C_1

and the percent of time by NT (C_4, d_{10})/NT (C_1, d_1). These available output summaries from FRANCO are valuable in the risk assessment procedure as they give information on whether the instream pesticide concentration exceeds specific laboratory determined LC50 conditions.

If more than one LC50 condition is of interest, then each can be considered separately using the above approach. In that case care in the interpretation of the results is necessary because of possible double counting of times and events. An alternative summary termed global exceedance is given to eliminate double counting. Global exceedance is based on the same concept as an LC50 function. An LC50 function can be defined by specifying pairs of concentration and duration values based on LC50 experiments. By connecting these pairs with straight line segments and extending the function in a reasonable manner at each end, a function is defined such that an event defined by a particular concentration level with a particular duration can be classified as exceeding or not exceeding the function, i.e., exceeding an LC50 value (see Figure 6). An event exceeds the LC function when the concentration defining the event and the duration of the event results in the pair falling above and to the right of the function. For the example data three events exceed LC function 1 (see Figure 6):

However, all three events occur during the same time period of the study, i.e., they consist of different slices of the same pesticide concentration peak. The global exceedance summary eliminates this double

TABLE 4. GLOBAL EXCEEDANCE SUMMARY

Ending Time Step	Number of Time Steps	Event Concentration
19	17	C_4
17	6	C_{10}
15	2	C_{15}

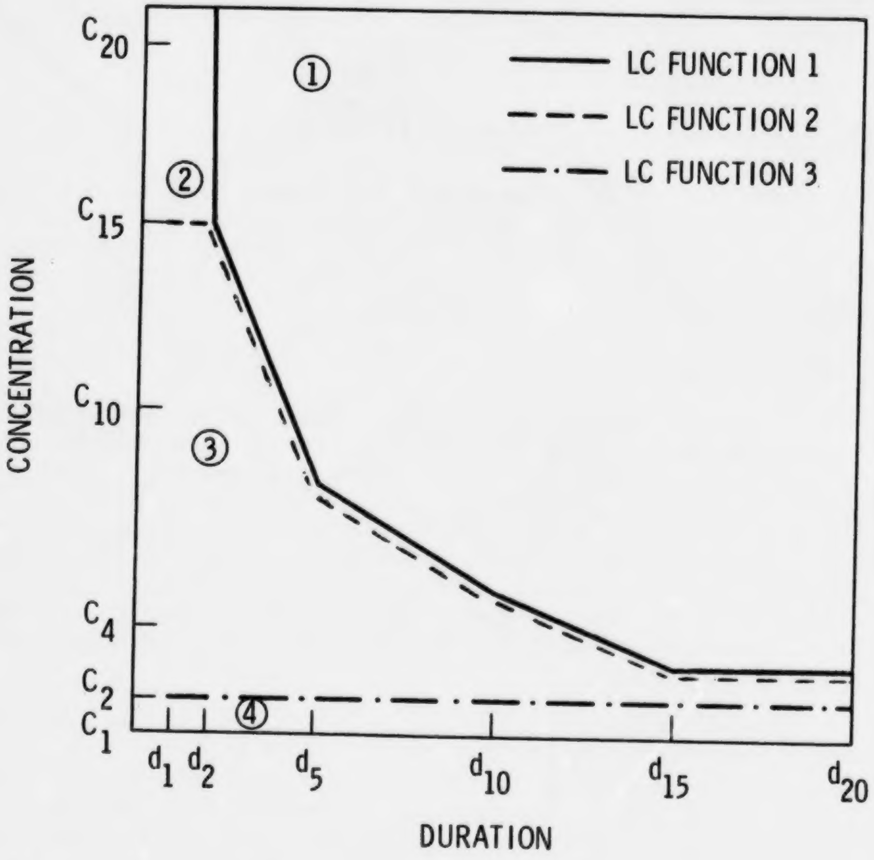


Figure 6. Example of functions used for global exceedance summary

counting by reporting only those events with the lowest concentrations that occur in different pesticide peaks. In this case only the event defined by C_4 is reported for LC function 1 in Figure 6. A summary is given of the number of non-overlapping events above the LC function, the time during the study spent above the LC function, expressed as time and as a percent of the total study period.

By selecting different LC functions it is possible to differentiate between short-term high concentration pesticide peaks and long-term low concentration peaks. By specifying the LC function to be the model cutoff concentration for all durations, as in LC function 3, the location of each pesticide occurrence instream can be determined as well as the global exceedance summary information. Figure 6 shows three LC functions which split the concentration-duration space into four non-overlapping regions (Numbered 1 to 4). The percent of time spent in each region can be determined from the global exceedance percent summary. First LC function 1 is exceeded 42.5 percent of the time, LC function 2 is exceeded 45% of the time and LC function 3 is exceeded 87.5 percent of the time. Therefore, during the study period the time spent in each region is:

Region 1	42.5%
Region 2	2.5%
Region 3	42.5%
Region 4	12.5%

An interpretation of these numbers might be that 12.5% of the time (Region 4) no significant pesticide concentration was present in the stream. For 42.5% of the time (Region 1), there are lethal impacts on fish. For 45% of the time (Regions 2 and 3), there are potential but unknown lethal and sublethal impacts on fish.

Risk Assessment

The risk assessment procedure provides a basis to predict the probability of lethality or sublethality affecting a given species from aquatic exposure to a particular pesticide. Two parameters have been chosen to describe the risk analysis probability curves. These are the use of LC50 data to generate the median acute toxicity curve and the maximum acceptable toxicant concentration (MATC) to describe the effect-no effect boundary for chronic toxicity. Because of the difficulties involved with field studies, such as keeping track of the organisms and eliminating food-chain interactions, bioassays and toxicity testing have largely been confined to special laboratory aquaria.

Most laboratory procedures limit organism exposure to the water soluble pesticide fraction. Ingestion of pesticide on food particles is eliminated as an exposure mechanism because the organism is usually not fed during short-term tests. The organism in its natural environment may ingest pesticide sorbed onto food and debris surfaces. Bottom dwelling invertebrates and filter-feeding fish are also in contact with and may ingest sediment and its corresponding adsorbed pesticide. Ingestion as a secondary route of intake is known in some cases to add to toxic effects thus complicating direct comparison of field studies with laboratory evaluations.

An organism in the wild has many more potential environmental stresses than the laboratory animal. The field animal may be subject to starvation, poor water quality, temperature changes, predation, and various chemicals in addition to the pesticide of concern. Its response to the pesticide may be more or less severe than those in laboratory studies. The additional stress may act in combination with other factors enhancing the chemical's toxicity; on the other hand, the organism may prove better able to tolerate or resist the poison because of prior adaptations. Migration and avoidance may allow mobile species to minimize exposure. Consequently, it is stressed that direct application of laboratory results to field situations must be made cautiously with an understanding of the underlying assumptions involved.

Investigators have used different techniques in their measurements of LC50 values. The most accepted acute method is the flow-through test where pesticide concentrations are actually measured. Many static bioassays have been conducted and some published test results are based on calculations of pesticide concentration. Results from these different techniques are not always comparable.

The Office of Water Planning and Standards, U.S. Environmental Protection Agency has proposed the use of LC50 correction factors to standardize values to the 96-hour flow-through bioassay of measured concentration (EPA, 1979). While these factors are not final regulations and are subject to change, this sort of approach may be taken where standardization of data is warranted. The use of actual observed 24-, 48-, 72-, and 96-hour LC50 data and of flow-through bioassays of measured concentrations is preferred when available.

LC50 values derived from flow-through tests showed a geometric mean of concentrations to be 71% of those measured in static tests. Consequently, the Office of Water Planning and Standards has suggested the use of this figure to standardize static results to flow-through conditions (i.e., 0.71 multiplied by the static results approximates the concentration using the flow-through method). Likewise, their study of LC-50 values based on actual measured chemical concentrations versus calculated chemical concentrations (based on the amount of toxicant added to the known amount of water rather than direct measurement after the toxicant is in solution) revealed an additional common discrepancy. Calculated values tend to be higher than actual measured concentrations. Calculated data may be standardized to reflect the probable equivalent measured concentrations by multiplying calculated data by 0.77.

In the same article the Office of Water Planning and Standards offered a procedure for standardizing 24-, 48-, and 72-hour bioassays to 96-hour LC50. This can be accomplished by multiplying these values by the following factors to estimate its 96-hour LC50 data point.

Given: 24-hr LC50, multiply by 0.66 to get 96-hr LC_{50}
48-hr LC50, multiply by 0.81 to get 96-hr LC_{50}
72-hr LC50, multiply by 0.92 to get 96-hr LC_{50}

Diverse pesticide and biological properties such as lag-time and secondary mechanisms of action are not considered. Use of these factors implies a fixed relationship between lethality and time. While this assumption is not specifically correct for any particular pesticide, its use allows for relative comparison of toxicities cited in studies of different duration.

Construction of a median lethality curve requires input of LC50 concentrations over a variety of time durations. A time concentration mortality (time-LC50) curve carried out to the lethal threshold concentration level is ideal for this use and should be applied when available. More commonly, a lethality graph must be approximated from incomplete sets of LC50 data. Toxicity data typically found in the literature are one or more distinct LC50 values. Finding values for specific aquatic species may prove to be difficult, or impossible, particularly for chemicals of relatively low toxicity. Appendix B includes tables of pesticide toxicity data for certain organic compounds. Other data sources include the EPA Office of Pesticide Programs, EPA pesticide registration files, and pesticide manufacturers.

The accuracy of the time LC50 curve improves by increasing the number of LC50 data for different time intervals. Confidence limits around LC50 values are often listed and should be recorded for later use. A description of testing conditions should also be recorded with the mortality values, as they may be useful in the selection of the most appropriate data points. When several investigators have reported conflicting values for a particular pesticide and species, the discrepancies may be the result of specific conditions which may be discussed in the text of the article. The LC50 value under conditions corresponding more closely to case study conditions would be the logical choice.

Frequently, sufficient LC50 data do not exist to properly estimate a curve. Figure 7 illustrates the procedure for estimating needed FRANCO input data points when these are not available. When only one or two values are available for a particular species, one of several methods can be employed to approximate missing values. The first of these is to use the slope of the toxicity curve of a related species for the same chemical. This principle is demonstrated on page A-5 in Appendix A. Appendix B provides a phylogenetic chart to indicate the genetic relationships of various fish species. A species of the same genus is the preferred choice for use of slope data, though it may be necessary to use those related at the family level. A second method for estimating missing data is to use the geometric mean of the toxicity slopes of other species for the same pesticide as shown on page 90. Finally, the geometric means discussed above in regard to LC50 standardization factors may be used to approximate unknown values. The reciprocals of the ratios correcting values to a 96-hour LC50 can be used to estimate values for 24-, 48-, and 72-hours given a 96-hr LC50. Note that these are approximations and may not reflect any particular set of experimental values. An example of this method is shown on page 91.

In the event that no data can be found for a particular species, an approximation of the curve may be derived from LC50 value trends given for other species for the same pesticide. Again, the selection of genus related species is most appropriate. Assignment of a range in terms of LC50 values is preferred where insufficient data requires the use of other family related species. A geometric mean may be calculated from this range for a more simplistic approach to probability modeling. If no values exist for other species of the same family, it may be useful, though perhaps less

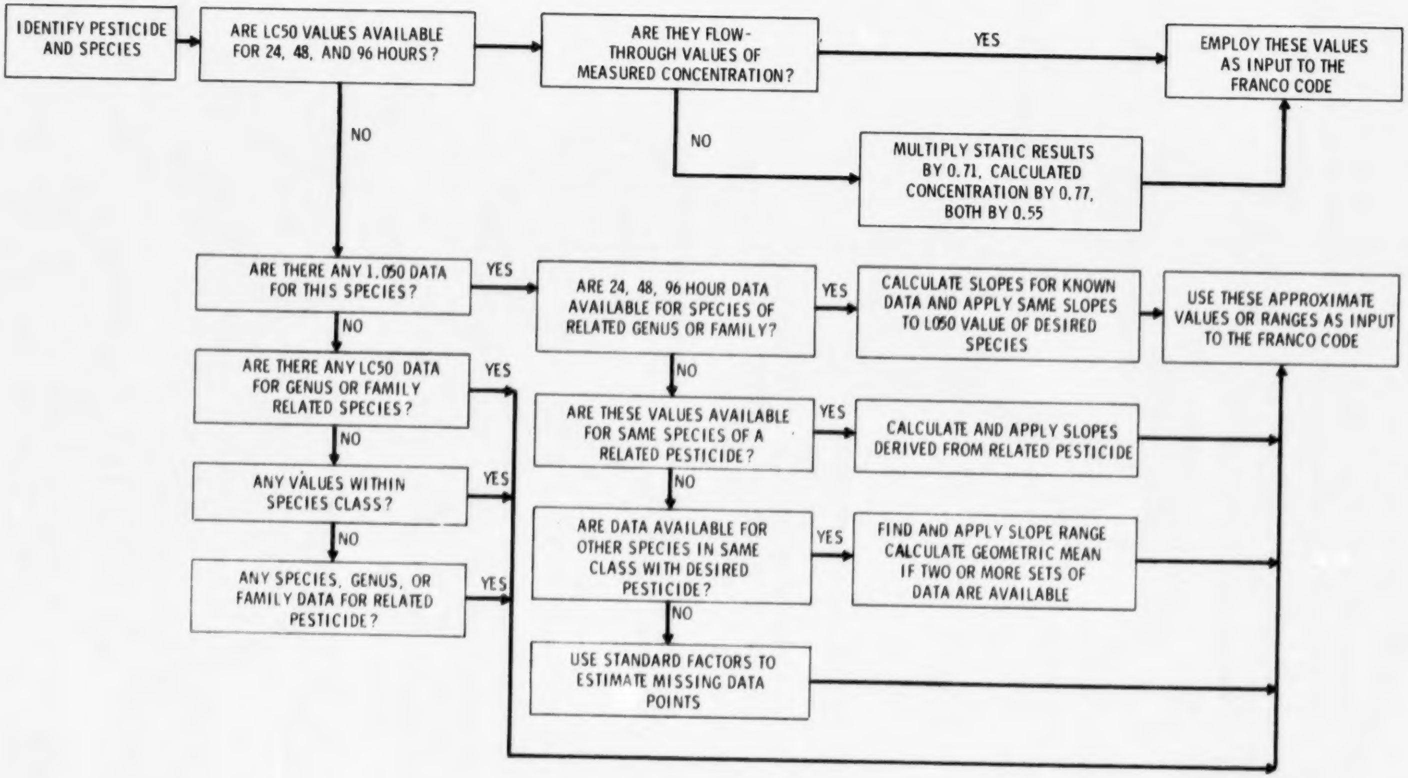

IDENTIFY PESTICIDE AND SPECIES
ARE LC50 VALUES AVAILABLE FOR 24, 48, AND 96 HOURS?
ARE THEY FLOW-THROUGH VALUES OF MEASURED CONCENTRATION?
YES
EMPLOY THESE VALUES AS INPUT TO THE FRANCO CODE
NO
NO
MULTIPLY STATIC RESULTS BY 0.71, CALCULATED CONCENTRATION BY 0.77, BOTH BY 0.55
ARE THERE ANY LC50 DATA FOR THIS SPECIES?
YES
ARE 24, 48, 96 HOUR DATA AVAILABLE FOR SPECIES OF RELATED GENUS OR FAMILY?
YES
CALCULATE SLOPES FOR KNOWN DATA AND APPLY SAME SLOPES TO LC50 VALUE OF DESIRED SPECIES
USE THESE APPROXIMATE VALUES OR RANGES AS INPUT TO THE FRANCO CODE
NO
ARE THERE ANY LC50 DATA FOR GENUS OR FAMILY RELATED SPECIES?
YES
NO
ARE THESE VALUES AVAILABLE FOR SAME SPECIES OF A RELATED PESTICIDE?
YES
CALCULATE AND APPLY SLOPES DERIVED FROM RELATED PESTICIDE
NO
ANY VALUES WITHIN SPECIES CLASS?
YES
NO
ARE DATA AVAILABLE FOR OTHER SPECIES IN SAME CLASS WITH DESIRED PESTICIDE?
YES
FIND AND APPLY SLOPE RANGE CALCULATE GEOMETRIC MEAN IF TWO OR MORE SETS OF DATA ARE AVAILABLE
ANY SPECIES, GENUS, OR FAMILY DATA FOR RELATED PESTICIDE?
YES
NO
USE STANDARD FACTORS TO ESTIMATE MISSING DATA POINTS

Figure 7. Procedures for assigning LC50 values for model input.

justifiable, to use less taxonomically related species to determine a likely toxicity range.

If no aquatic lethal toxicological data is accessible for a particular pesticide, the use of data from other related pesticides may be an indication of probable toxicity if biological data shows similarity. One should seek out the same organism as is being studied for a toxicity range. These approximation techniques only suggest trends and are used solely for model continuity.

One further method describing the lethality curve is presented, but its proper application has not been determined. It is based on the apparent hyperbolic character of the LC50 curve. A computational method of determining duration-concentration values on this curve, particularly for the lethal threshold concentration, is discussed by Dawson et al. (1974), and refers to a mathematical formula described by Wuhrmann (1952) as

$$(C-C_s)^n(d_m-d_s) = K$$

where

C = concentration of toxin
C_s = concentration threshold
d_m = response time of fish
d_s = threshold of response time
n,k = constants

The method may be limited to pure compounds or formulations demonstrating only one mechanism for lethality. Data points must lie in an hyperbolic pattern having both horizontal and vertical assymptotes on a graph of time versus concentration. Use of this formula may have an important application as a method of extending the lethal curve beyond the last experimental point.

The mechanism for predicting potential sublethal effects is based on the use of the experimentally derived MATC range. The MATC range is located between the highest value showing no detectable harmful effects and the lowest values displaying some observable effect.

While recent focus on chronic data has greatly expanded its availability, MATCs have not yet been generated for the majority of pesticides. The requirement for a MATC range is paramount to the sublethal assessment process. Figure 8 illustrates the alternatives when no MATC has been published for a particular pesticide and aquatic species. Where considerable chronic data is available on long-term exposure, the MATC range can be simply written as the interval between the highest no effect level to the lowest effect level. If the tests were not run specifically to establish such limits, this range may be wider than necessary.

Where neither MATC nor adequate chronic values are obtainable for the species of concern, data for other species' response to the same pesticide

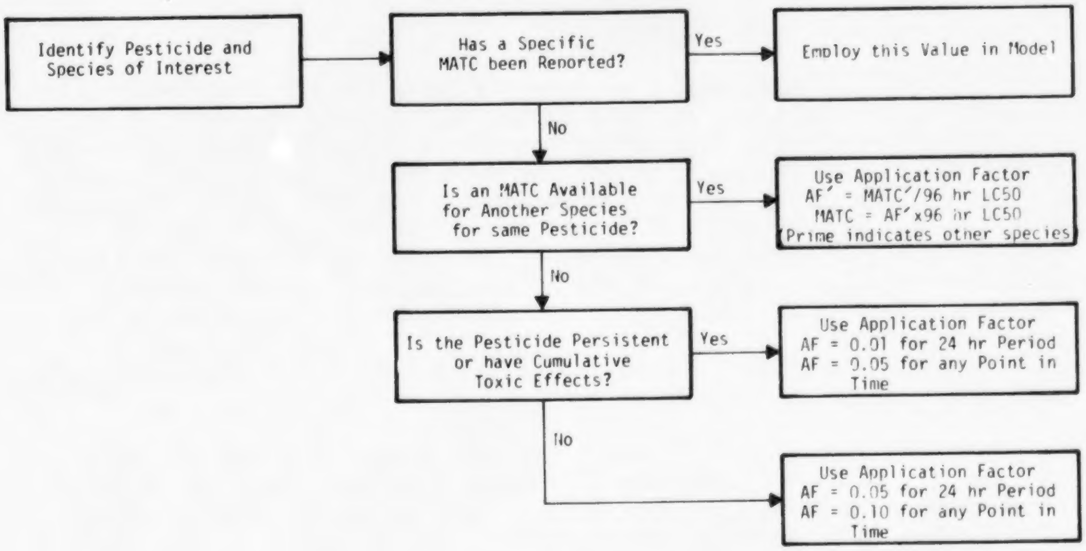

Identify Pesticide and Species of Interest
Has a Specific MATC been Reported?
Yes
Employ this Value in Model
No
Is an MATC Available for Another Species for same Pesticide?
Yes
Use Application Factor
AF′ = MATC′/96 hr LC50
MATC = AF′x96 hr LC50
(Prime indicates other species)
No
Is the Pesticide Persistent or have Cumulative Toxic Effects?
Yes
Use Application Factor
AF = 0.01 for 24 hr Period
AF = 0.05 for any Point in Time
No
Use Application Factor
AF = 0.05 for 24 hr Period
AF = 0.10 for any Point in Time

Figure 8. Procedure for assigning chronic toxicity input data.

may be applied. The existence of a correlation between the 96-hour LC50 and the MATC has been noted in the Water Quality Criteria - 1972 (WQC 1972). An application factor (AF) may be derived from known 96-hour LC50 and MATC values and may be applied to other species exposed to the same pesticide to estimate its MATC. The apparent similarity of the ratio of MATC to a 96-hr LC50 for different species for a particular pesticide has been discussed by Eaton (1973). The measured MATC range is divided by the 96-hour LC50 for the known species to calculate an Application Factor (AF) range.

MATC Range/96-hr LC50 = Application Factor Range

The product of this AF and the 96-hour LC50 of the species of concern can be used to estimate its MATC.

AF Range x 96-hr LC50 = MATC

The following information, as explained above, should now be ready for computer analysis of each pesticide and aquatic species under consideration:

Lethality: 24-hr LC50
48-hr LC50
96-hr LC50
Other LC50 points given by toxicological studies
Incipient LC50 if given or calculated
Confidence intervals if available.

Sublethality: MATC range
MATC point

Ideally, all these points will be available for the graphing of lethality over both short and long exposures. However, in addition to the lack of one or more data points describing the LC50 concentrations at points 24, 48, and 96 hours, several assumptions are required to complete the curve. The curve must be defined between the point on the vertical axis (C_o, d_o) and the shortest lethal data point and also beyond the longest lethal or sublethal data point. Input of the minimum time to achieve a lethality response at high concentrations (t_m) is required. Frequently this value lies between one and six hours, thus allowing for the assignment of a reasonable but arbitrary t_m. Sometimes it may be two days or more. Experimental data should be used where available to resolve this upper end of the LC50 curve.

The LC50 line from d_o to the first data point may be most justifiably dealt with by extending the LC50 curve from the concentration at the first known data point (C_1) horizontally back to the ordinate (Figure 9). This assumes that any value greater than C_o (which equals C_1) exceeds the LC50 line and is therefore included in the medium lethal zone. This assumption results in a conservative estimate for this section of the curve.

A second approach for handling this area assumes no lethality exceeding 50% occurs at any concentration for a species exposed less than time equal to d_1. It is represented by a vertical line extended above (C_1,d_1) as illustrated in Figure 10. This method is the least conservative measure of lethality for the duration $d < d_1$. The curve for this section may be modeled in some alternate fashion if enough evidence exists to justify a different procedure. An example of such manipulation is defining a slope from some point $C_o > C_1$ to point C_1. The lethal curve probably approaches the ordinate at $C > C_o$ in a hyperbolic fashion.

Straight line segments have been used to define the LC50 curve between the known points. An incipient LC50 value at a given time covered within the time plot may be considered the final known point where it has been given or calculated. The section between the last known point and the LC50 concentration at the arbitrary end of the curve is the second area of uncertainty.

This uncertainty has been dealt with in two ways. The first procedure is to extend the final known LC50 value horizontally to the end (Figure 11). This assumes the incipient LC50 has been reached. Sometimes, however, the lethality curve continues a significant negative slope past the last known value, especially when the effects are cumulative. In this case the lateral extension of the last concentration value may vastly underestimate the potential for lethality.

The second procedure is a conservative lethality estimate. The LC50 and MATC parameters are combined in a single relationship to assess the

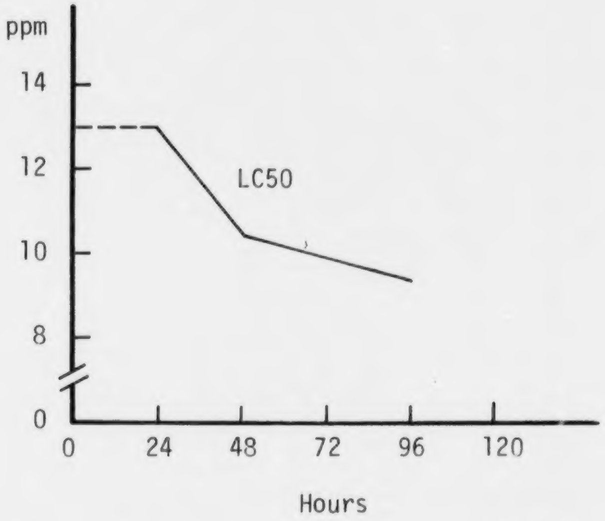


Figure 9. Horizontal extrapolation of the LC50 curve to origin.

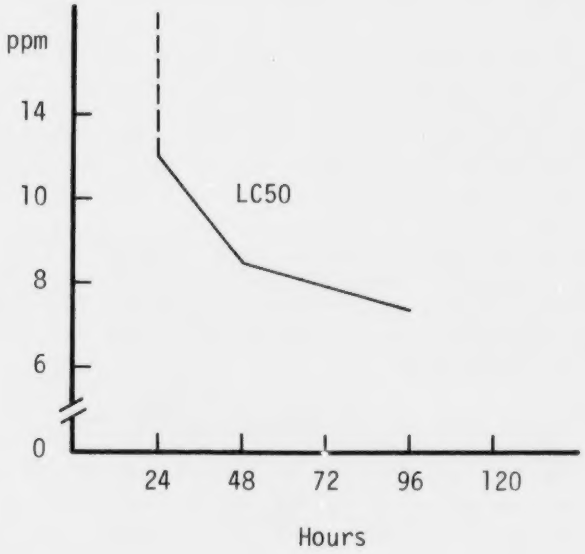


Figure 10. Vertical extrapolation of the LC50 curve

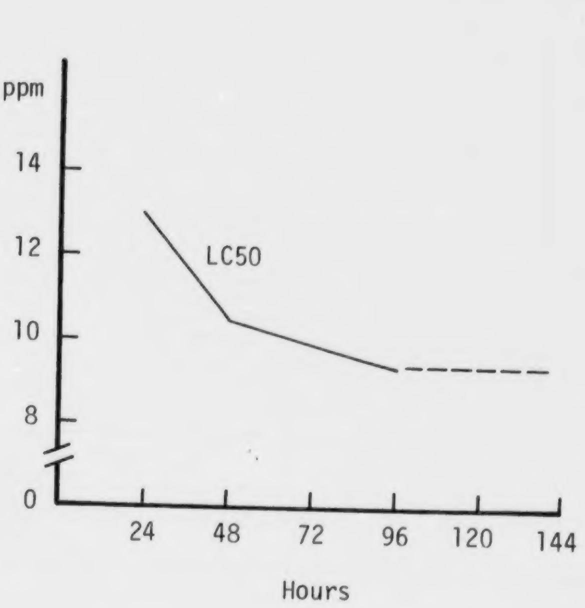


Figure 11. Horizontal extension of the LC50 curve.

probability of short-term median lethality or long-term effects. This curve is illustrated in Figure 12. A value of 96 hours has been selected to merge the LC50 curve with the MATC line because of its frequent usage as a separation for acute and chronic toxicity. Another time may be preferentially selected for merging the curves if the LC50 curve is known to level out at some point considerably before or after 96 hours.

FRANCO accepts a maximum of six pairs of concentration-duration points to define each curve. Where more than six pairs are available and necessary for modeling, these values may be incorporated into two or more curves. The areas exceeding the curves at all points or between all line segments can then be estimated.

The choice of the input curves depends on the needs of a methodology user. Some of the possible curves are illustrated in Figures 13a to 13d. Interpretation of the curves requires an understanding of the assumptions they represent. The curves a, b, c, and d in Figure 13 are offered as the most informative at this time. Additional curves may be generated as desired for the time frame deemed most important. For example, the curve may be described and its probability estimated for a duration longer than 48 or 96 hours.

If no chronic data or MATC values can be obtained, an arbitrary application factor based on the chemical's persistence and acumulation tendencies as discussed in the WQC-72 standard may be used. WQC-72 defines persistent as having a half-life greater than four days. If the compound is known to be persistent or be cumulative in its effects, use 0.01 as the standard application factor. If it is neither persistent or cumulative in

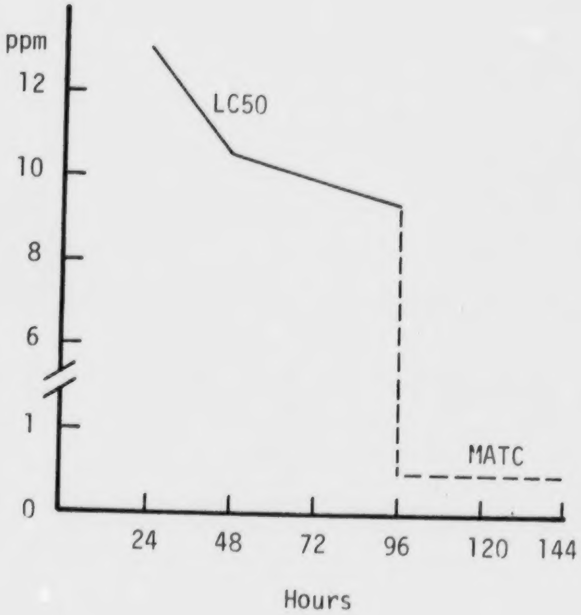


Figure 12. Combination of the LC50 curve with the MATC value.

action, an AF of 0.05 should be applied. Concentrations between 0.01 and 0.05 of the 96-hr LC50 should not be exceeded for more than 24 hours for the non-persistent chemicals.

The MATC range for experimentally derived data may be converted to a point for convenient computer manipulation. Two options exist for its calculation. The first is to take the geometric mean of both extreme values as the MATC value. The second is to choose one of the MATC range limits for the distinction. Use of the highest no effect value is the most conservative method.

The FRANCO output is a summary of concentration information based on certain physical and chemical characteristics. It is an important tool to aid the interpretation of the potential effects of a chemical on a given species. However, there are other factors that may be critical to a specific assessment. The FRANCO output does not reflect biological effects other than toxicity and cannot reflect fish behavior in avoiding or preferring the affected area, induced sensitivity or resistance to the chemical(s), life stages during which sensitivity is greatest or least, synergistic or antagonistic effects from other chemicals in the water, and a variety of other "real world" possibilities. It is up to those interpreting the results to consider these factors along with the concentration summary provided by FRANCO to assess associated risks of pesticides.

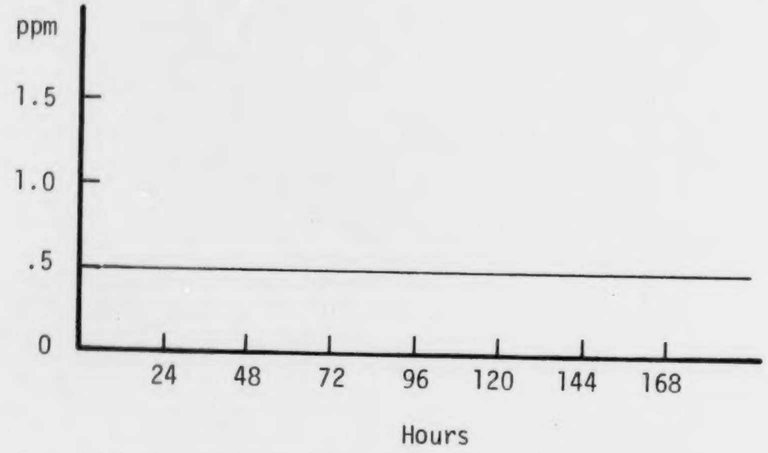


Figure 13a. The MATC line converted from MATC range.

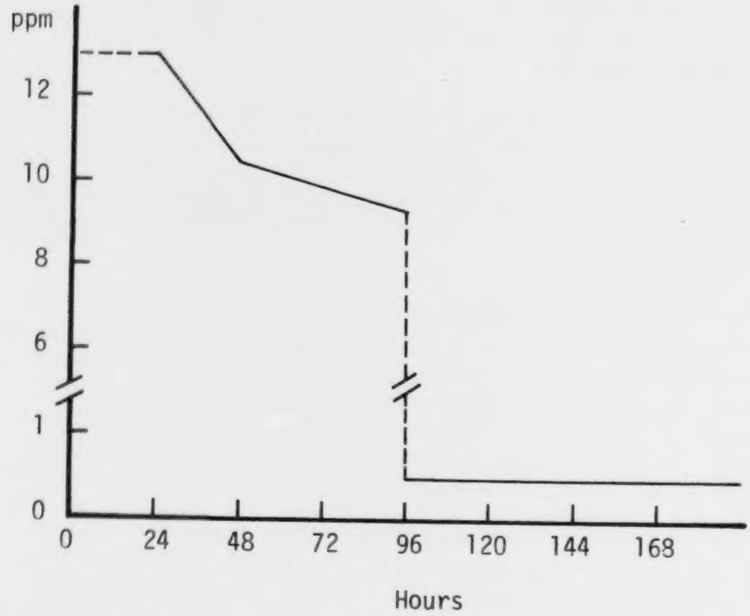


Figure 13b. Conservative estimate of lethality using MATC line.

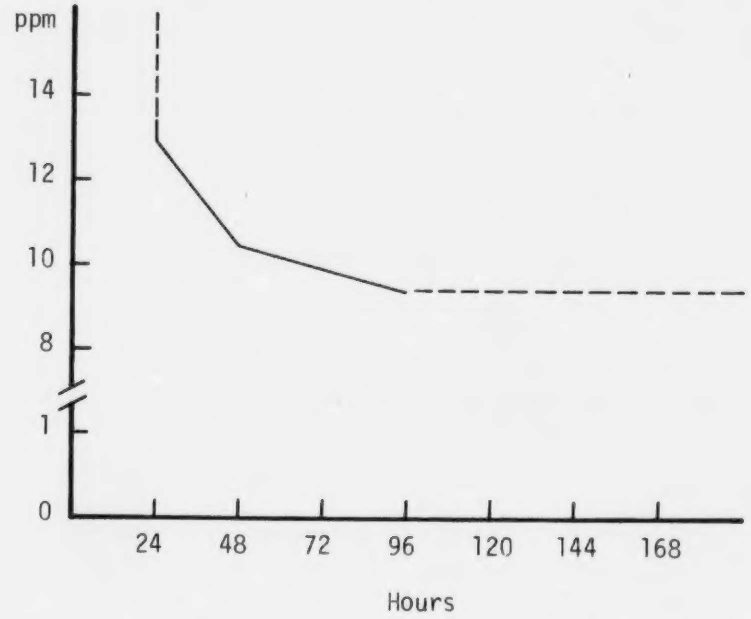


Figure 13c. Least conservative estimate of lethality.

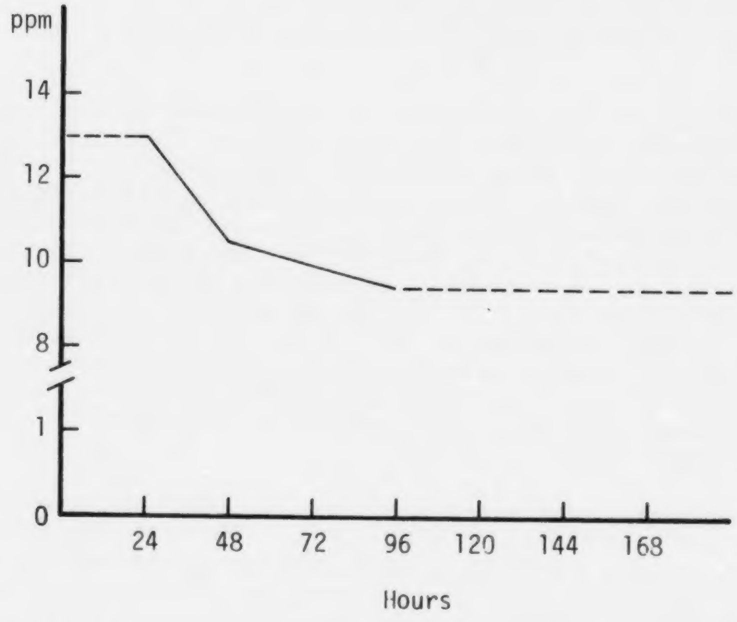


Figure 13d. Alternative representation of lethality in unknown regions.

SECTION 5

APPLICATION OF METHODOLOGY

GENERAL REMARKS

The CMRA Methodology described in this report is the first attempt to integrate mathematical models with statistical analysis and risk assessment procedures to produce a comprehensive nonpoint source pollution assessment tool for pesticides. For this reason, it was necessary to evaluate the soundness of the methodology by applying it to an agricultural watershed and receiving streams. In addition to evaluating the soundness, there were other important reasons for the test application. Mathematical-model-based methodologies generally require large quantities of detailed field data. Since data availability could be a constraint to the use of the methodology, the test application was used to help identify data requirements. A test application of the methodology also provided a means of developing a step-by-step procedure for its use (see Appendix A). Finally, the applicability, limitations, and required refinements of the methodology, as well as each of its components, were best identified through such an application.

The first step in the application of the CMRA methodology was to identify agricultural watersheds for which detailed field sampling programs had been or are currently being conducted. Representatives from the Environmental Protection Agency, the United States Geological Survey, the United States Department of Agriculture Science and Education Administration (previously the Agricultural Research Service) were contacted, along with a number of state environmental agencies and university researchers to identify potential data sources. This survey showed that pesticide data have classically been collected at two levels: 1) on large watersheds or river basins usually several hundred square kilometers in size or 2) on small field sites or test plots which are usually less than 5 to 10 ha in size. Only recently have field data collection programs been initiated on moderate size watersheds.

One such program is being conducted by Iowa State University (ISU) on the Four Mile Creek watershed in central Iowa. The basic objectives of the field sampling program are 1) to collect data for use in testing and refining ARM and 2) to conduct complimentary model-oriented research related to nonpoint pollutants from agricultural lands (Baker et al. 1979). The transport of sediment, pesticides and nutrients by water is being studied in order to obtain a better understanding of the effect of agricultural activities on water quality and to improve the usefulness of models as tools for assessing alternative agricultural management systems. This three-year program, which began in 1975, involves cooperation among the Agricultural Engineering and Agronomy Departments at ISU; Hydrocomp, Inc.; and the EPA Environmental Research Laboratory, Athens, Georgia. Since the data generated under the Iowa State University study generally met the data requirements of at least the overland modeling portion of the methodology, the Four Mile Creek watershed was selected for testing purposes.

The Four Mile Creek watershed is located in northwestern Tama County, Iowa and covers an area of about 50.5 km^2. It is typical of the heavily cropped regions of Iowa, the major crops being corn, soybeans, oats and hay. Annual sediment yields for basins in this region are about 150 MT/km^2 for basins on the order of 50 km^2 in size and water yields average about 150 mm/yr (Baker et al. 1979). Farmers usually plow corn lands and disk bean lands in preparation for the next crop. Fertilizers are applied by all farmers and herbicides are applied by most.

Figure 14 shows a map of the Four Mile Creek watershed along with the locations of hydrologic and meterologic data collection stations. The sizes of the catchments being studied range from field sites on the order of 6 ha in area to the entire watershed. Precipitation is measured by a network of recording rain gages. Other meteorological data are collected at a weather station located near the watershed. Runoff, either as streamflow or overland flow, is measured at each of the gaging stations. In Four Mile Creek, there are two gaging stations maintained by U.S. Geological Survey. There is no permanent gaging station in Wolf Creek whose tributary is Four Mile Creek. Sediment, pesticides and nutrient sampling also occurs at each gaging station. Details of the field sampling study, including other aspects of the sampling program such as soil sampling for pesticides and nutrients and crop inventories are presented by Baker et al. (1979).

Since the purpose of the methodology application to Four Mile Creek watershed was to evaluate the methodology and not to perform a complete assessment, only a portion of the watershed was used. This area is shown in Figure 15 as hatched catchments along with the Four Mile and Wolf Creeks; Wolf Creek is a tributary of the Cedar River. For the purpose of modeling runoff, sediment and pesticide contributions to Four Mile Creek, the watershed area was subdivided into the three catchments: the Gladbrook (344 ha), the northern catchment (660 ha), and the southern catchment (440 ha)(see Figures 14 and 15). The movement of sediment and pesticide were simulated over a 67.6 km reach of Four Mile and Wolf Creeks; the reach extended from upstream of the Lincoln gaging station to the mouth of Wolf Creek.

The pesticide selected for the test application was alachlor or Lasso (trade name). Alachlor is a preemergence herbicide used to control most annual grasses and certain broadleaf weeds. Alachlor is the most widely used herbicide in the Four Mile Creek watershed (Baker et al. 1979). Alachlor, applied at a recommended rate, has an average effective soil persistence of 6 to 10 weeks and is primarily degraded by microbial action and chemical breakdown (Weed Science Society of America 1979; Stewart et al. 1965). While alachlor will adsorb to colloidal particles in the

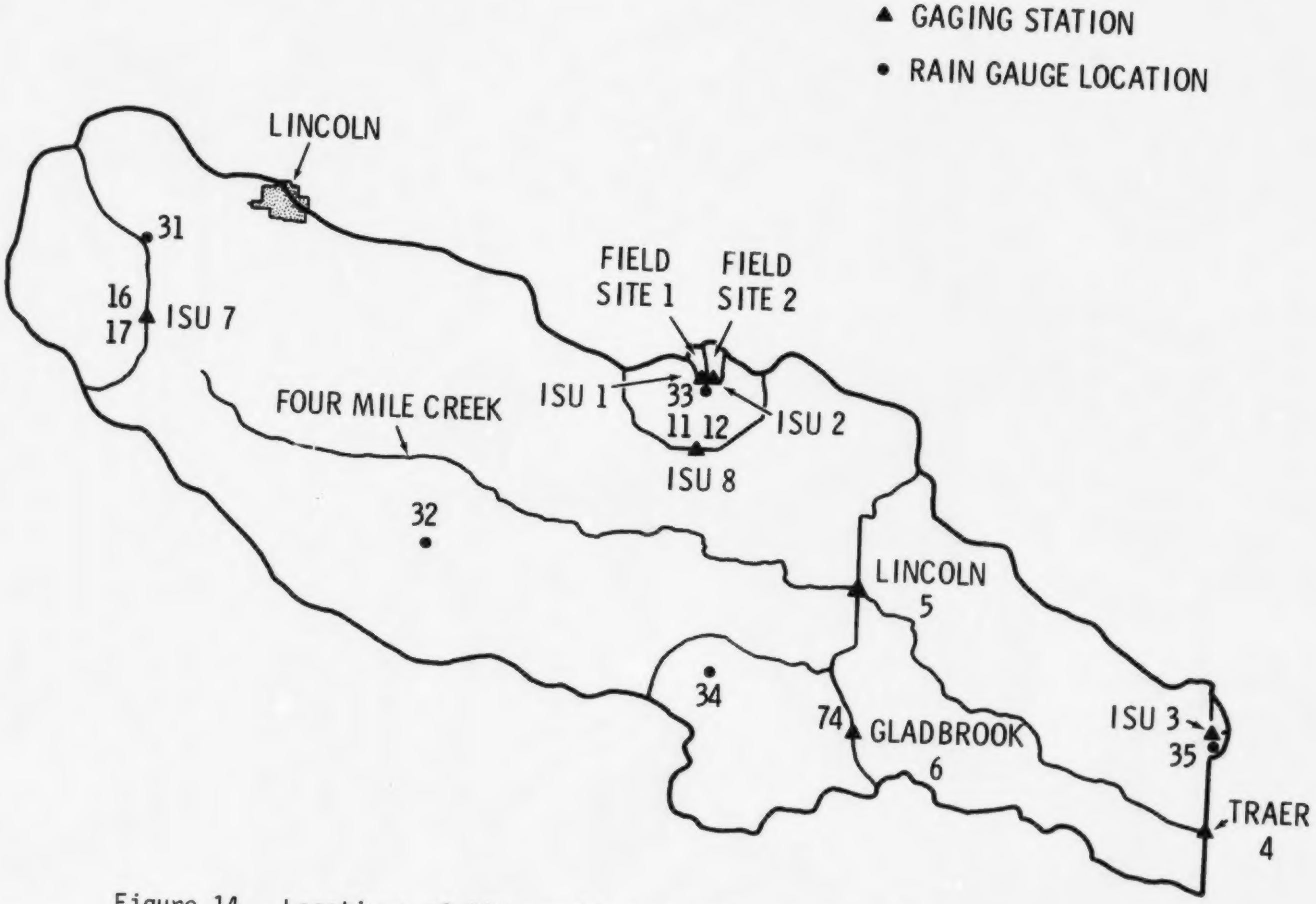

▲ GAGING STATION
● RAIN GAUGE LOCATION
LINCOLN
31
16
17
ISU 7
FIELD SITE 1
FIELD SITE 2
ISU 1
33
11 12
ISU 2
ISU 8
FOUR MILE CREEK
32
LINCOLN 5
34
74
GLADBROOK 6
ISU 3
35
TRAER 4

Figure 14. Locations of ISU sampling stations at four mile creek watershed.

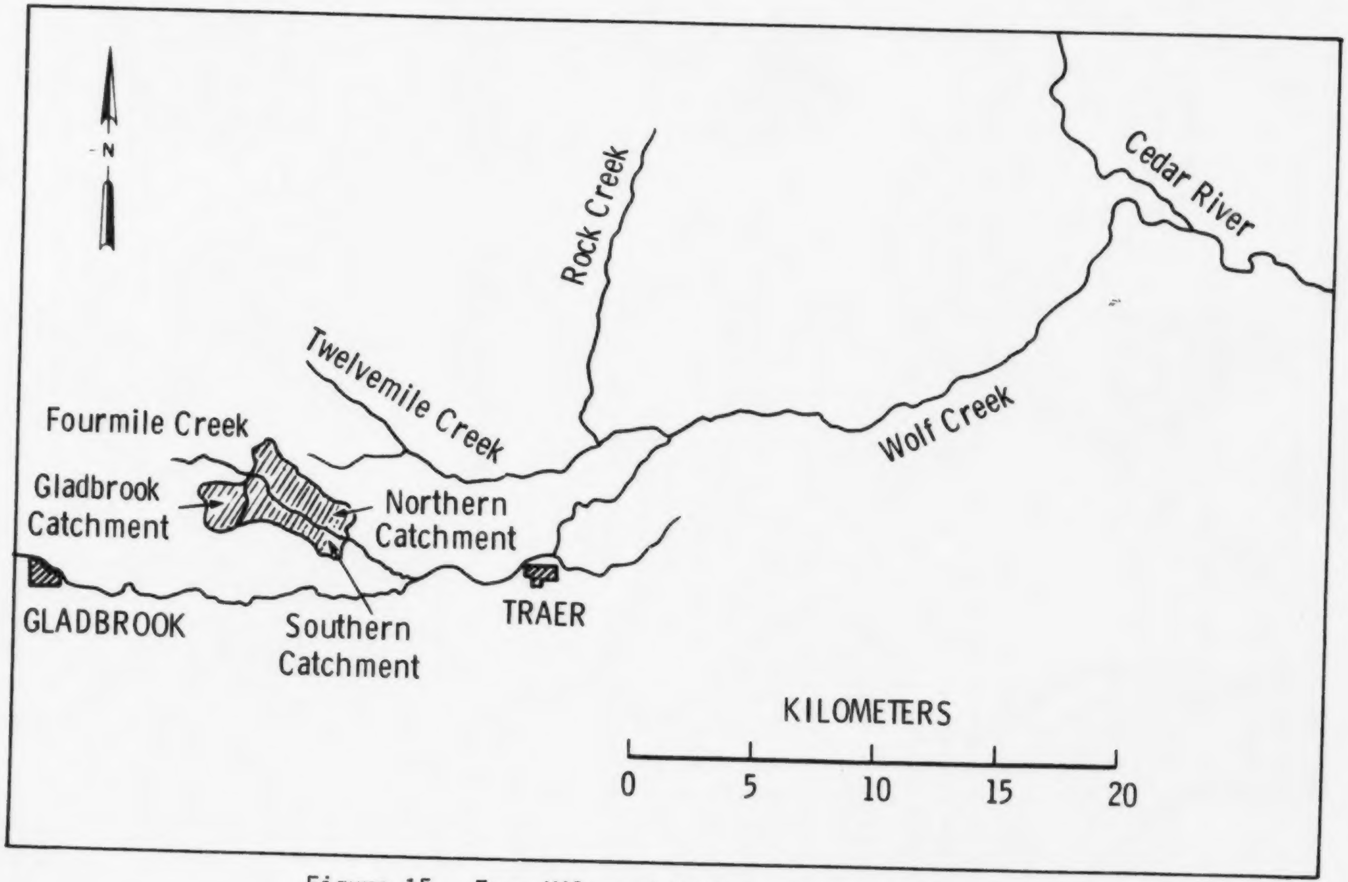

N
Rock Creek
Cedar River
Twelvemile Creek
Fourmile Creek
Wolf Creek
Gladbrook Catchment
Northern Catchment
GLADBROOK
Southern Catchment
TRAER
KILOMETERS
0
5
10
15
20

Figure 15. Four Mile and Wolf Creek in Iowa.

soil, it tends to be transported from agricultural lands mainly in a dissolved form. Its half-life in water depends on the aerobic character of the water body and its sediments. Alachlor on an aerobic sediment has a half-life of probably less than two weeks. Anaerobic sediment conditions speed the degradation process and result in a half-life of about four days.

Alachlor is moderate in its toxicity, causing acute effects at the 1 to 30 ppm range, and its level of bioconcentration is low for fish species tested. It has a solubility of 240 mg/l and a Kd value of 10 to 50 ml/g. As noted before, however, its persistence decreases with microbial interactions with sediments.

In order to obtain a long enough time history of pesticide concentrations in Wolf Creek for statistical analysis and risk assessment, a three year duration between June 1971 to May 1974 was selected. More details regarding the test application are given in the following discussions of each component of the methodology.

OVERLAND PESTICIDE MODELING

An evaluation of the ISU data showed that even though very few storms occurred during 1976 and 1977 due to drought conditions, the data for ISU Field Sites 1 and 2 (see Figure 14) were detailed and complete enough for an initial calibration of ARM. Since alachlor was applied only to ISU Field Site 1 in 1976, this catchment was selected for use in model calibration. Precipitation data from Rain Gauge No. 33 and meteorological data from the ISU weather station were input to ARM along with other data on catchment characteristics, crop growth and times of tillage and pesticide application. Initial values of model calibration coefficients were established by using the guidelines given in the ARM User's Manual (Donigian and Davis 1978).

Initial attempts to calibrate the hydrology coefficients on ISU Field Site 1 showed that no single set of coefficients could be selected to represent the highly variable runoff conditions caused by soil tillage at the site. The dramatic impact of tillage practices can be illustrated by comparing the measured runoff from Field Site 1 with that measured at Field Site 2. Field Site 2 is located next to Field Site 1 (see Figure 14) and, with the exception of cropping pattern, both sites have basically the same size, topographic characteritics, soil composition, and precipitation patterns. Field Site 1 has an area of 5.7 ha and was planted with soybeans in 1976, while Field Site 2 has an area of 7.6 ha and was planted with corn. In 1977 these crops were rotated. Table 5 presents a comparison of total runoff from both sites for each of the five major storm events which occurred in 1976 and 1977. Besides showing the impact that recent tillage operations have on reducing surface runoff, the comparison also shows that deeper tillage practices like plowing have a greater impact than disking. Similar observations on the effects of various tillage systems on soil and water loss from Iowa soils were reported by Laflen et al. (1978).

Future improvements to ARM should include the incorporation of tillage parameters into the hydrologic component of the model. Perhaps the infiltration coefficient (INFIL) could be increased at the time of tillage and then decreased to its nominal value through a linear or first-order decay scheme.

TABLE 5. RUNOFF COMPARISON FOR FIELD SITES NUMBER 1 AND 2

Storm Event	Rainfall (mm)	Field Site #1 Runoff (mm)	Field Site #1 Tillage Practice	Field Site #1 Date	Field Site #2 Runoff (mm)	Field Site #2 Tillage Practice	Field Site #2 Date
4/23/76	28	0.6	Plowed	4/5/76	6.0	Disked	4/2/76
5/29/76	29	3.8	Planted	5/19/76	11.4	Planted	4/28/76
6/13/76	37	8.1			1.2	Cultivated	6/7/76
4/19/77	20	4.5	Disked	4/19/77	0.0	Plowed	3/31/77
8/15/77	38	4.8			0.8		

Figures 16 through 20 show comparisons between the measured and simulated runoff for each of the five major storm events. The measured runoff for Field Site 2 and the average runoff for the two sites are included for comparison purposes. These figures show that although the model could not be calibrated to exactly simulate each event, the model does simulate the major trends fairly well. Much of the difference between measured and simulated values can probably be attributed to the impact of soil tillage.

While this impact is highly evident on field size areas, larger catchments (e.g., several hundred hectares in size) which are more heterogenous in terms of cropping and tillage patterns would not be as highly affected by tillage since all of the fields in a larger catchment would not be tilled at the same time or to the same degree. Since the ARM model was to be applied to areas larger than the Field Sites 1 and 2 in the test application, the calibrated hydrology coefficients for these field sites were tested by applying ARM to the catchment area above ISU Station 8 (see Figure 14). This catchment is about 30 times larger than the Field Sites 1 and 2 and closely approximates the sizes of the catchments selected for the test application (see Figure 15). While detailed runoff measurements were only taken during 1977 at Site 8, comparisons between measured and calculated flows indicated that several of the hydrology coefficients had to be slightly modified. The initial and modified values for each coefficient are listed below.

	Initial	Modified
UZSN	0.15	0.40
INFIL	0.10	0.03
INTER	0.70	1.50

Leytham and Johanson reported an earlier application of ARM to Four Mile Creek watershed (Leyham and Johanson 1979). Table 6 shows that their calibrated coefficients agree quite well with the coefficients obtained during this study. The only exceptions are those hydrology parameters

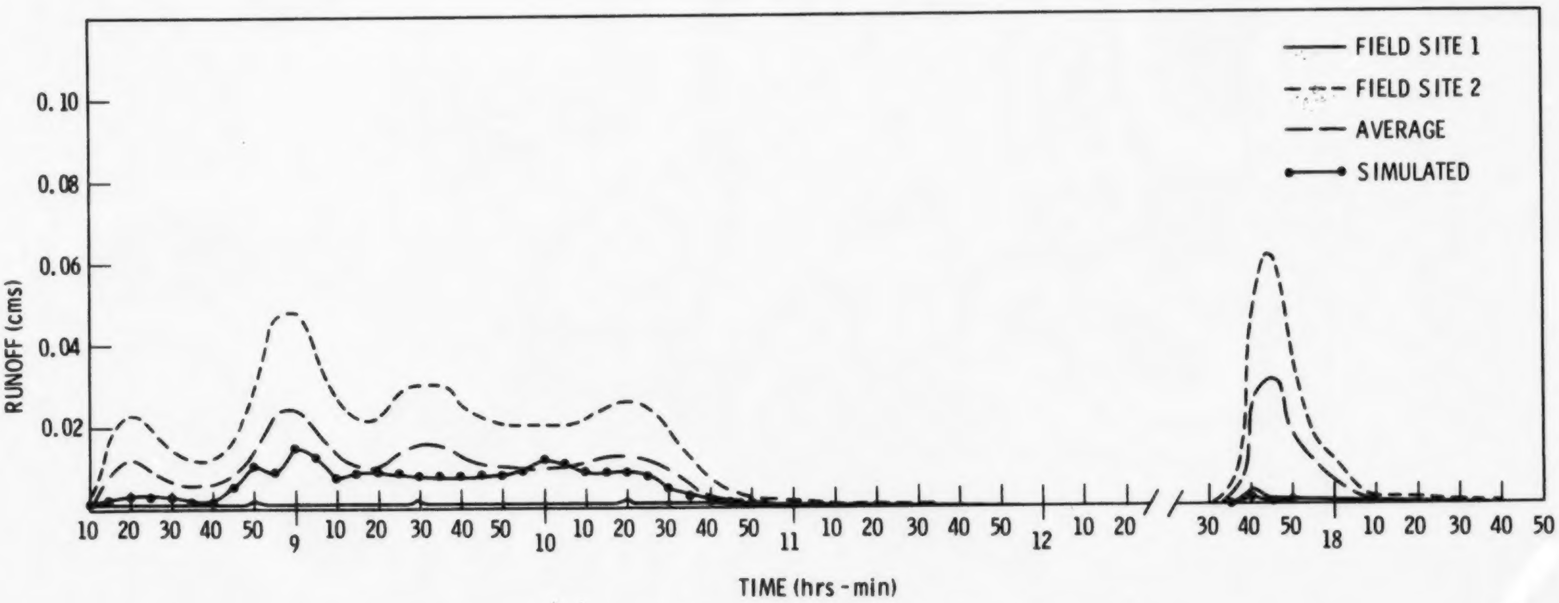


Figure 16. Simulated and measured runoff for the April 23, 1976 storm.

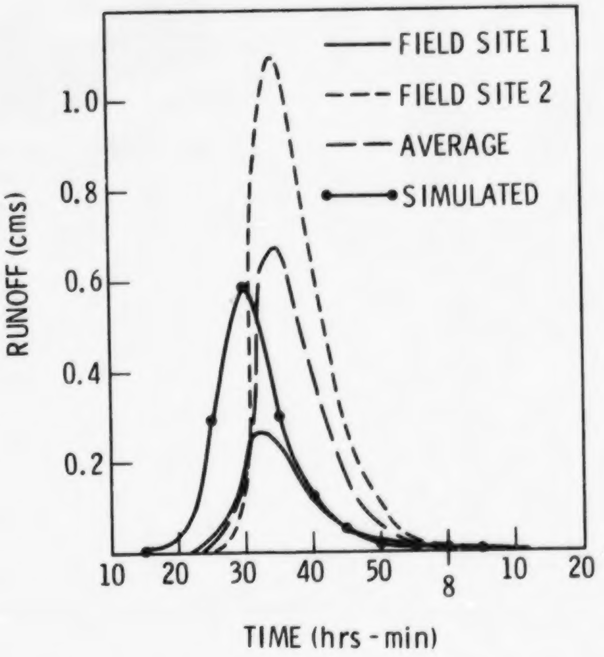


Figure 17. Simulated and measured runoff of the May 29, 1976 storm.

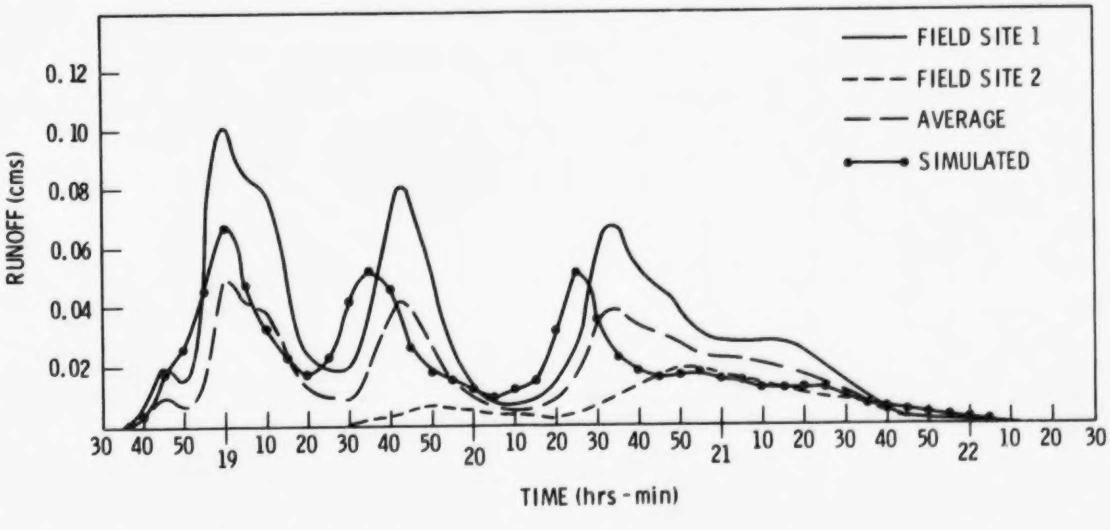


Figure 18. Simulated and measured runoff for the June 13, 1976 storm.

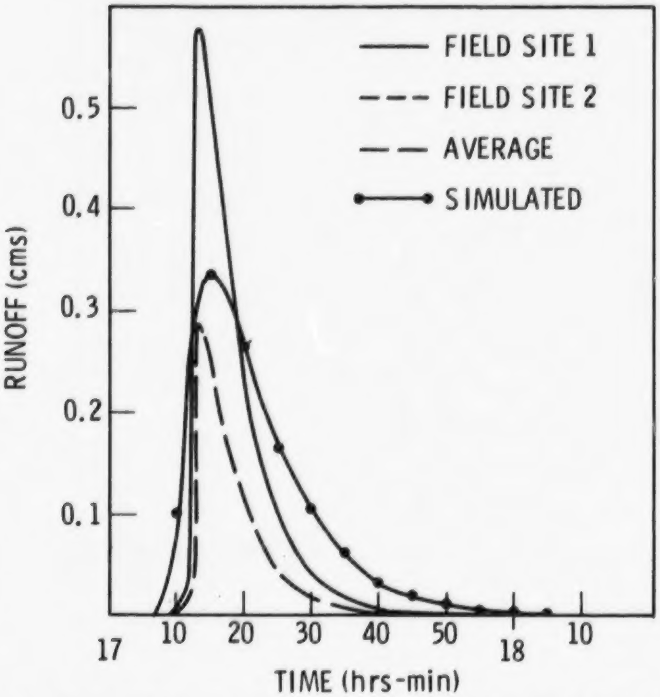


Figure 19. Simulated and measured runoff for the April 19, 1977 storm.

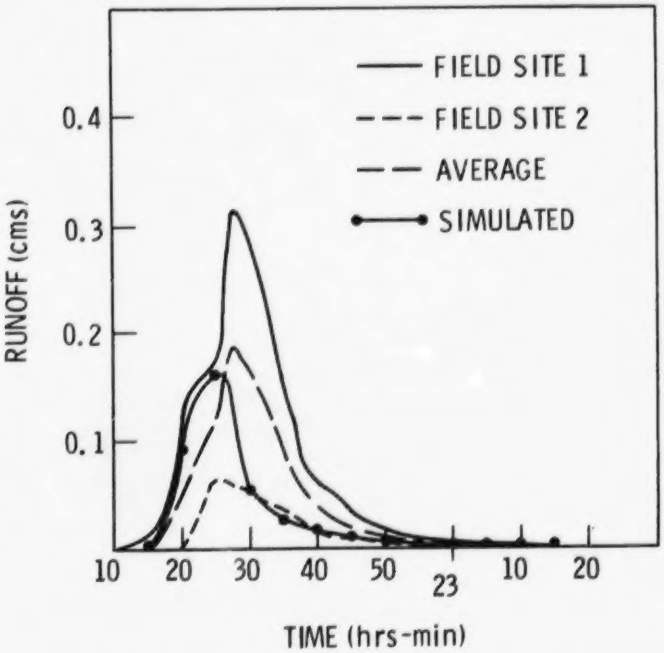


Figure 20. Simulated and measured runoff for the August 15, 1977 storm.

TABLE 6. COMPARISON OF HYDROLOGY COEFFICIENTS

Coefficient	Battelle-Northwest	Leytham and Johanson(a)
A	0.0	0.003
EPXM	0.12	0.09
UZSN	0.40	0.80
LZSN	8.0	7.8
K3	0.6	0.5(b)
K24L	1.0	0.35
K24EL	-	0.0
INFIL	0.03	0.035
INTER	1.50	3.5
L	200.0	520.
SS	0.065	0.060
NN	0.20	0.23
IRC	-	0.33
KK24	-	0.97
KV	-	1.0

(a) Average values for Segments 1, 2 and 3
(b) Average values for April through October

which are related to the groundwater component of runoff (i.e., IRC, KK24, K24EL, KV). The ISU Field Sites were too small to calibrate these parameters. As a result, the coefficients that could not be evaluated were supplemented with Leytham and Johanson's coefficients. Since no runoff data were collected at either field site during the winter months, the snowmelt coefficients could not be evaluated. Therefore, Leytham and Johanson's snowmelt coefficients were also used.

Figures 21 through 25 also show the measured and simulated sediment mass removal rates for each storm event. The model was calibrated to the Field Site 1 data since the two field sites were tilled at different times and to varying degrees. The sediment coefficients were calibrated to be consistent with the runoff results (i.e., if the simulated runoff was greater than that measured runoff for Field Site 1, the simulated sediment transport was also greater). Table 7 shows a comparison between the sediment coefficients obtained under this study and those obtained by Leytham and Johanson. Again, good agreement was obtained.

Soil-pesticide data collected during 1976 on Field Site 1 showed that the degradation rate for alachlor changed after the May 23, 1976 storm event which occurred only ten days after application. The degradation rates before and after the runoff event were about 0.08/day and 0.06/day, respectively. The first version of ARM does not have the multiple degradation rate option available in ARM-II. A value of 0.06/day was selected for the test application.

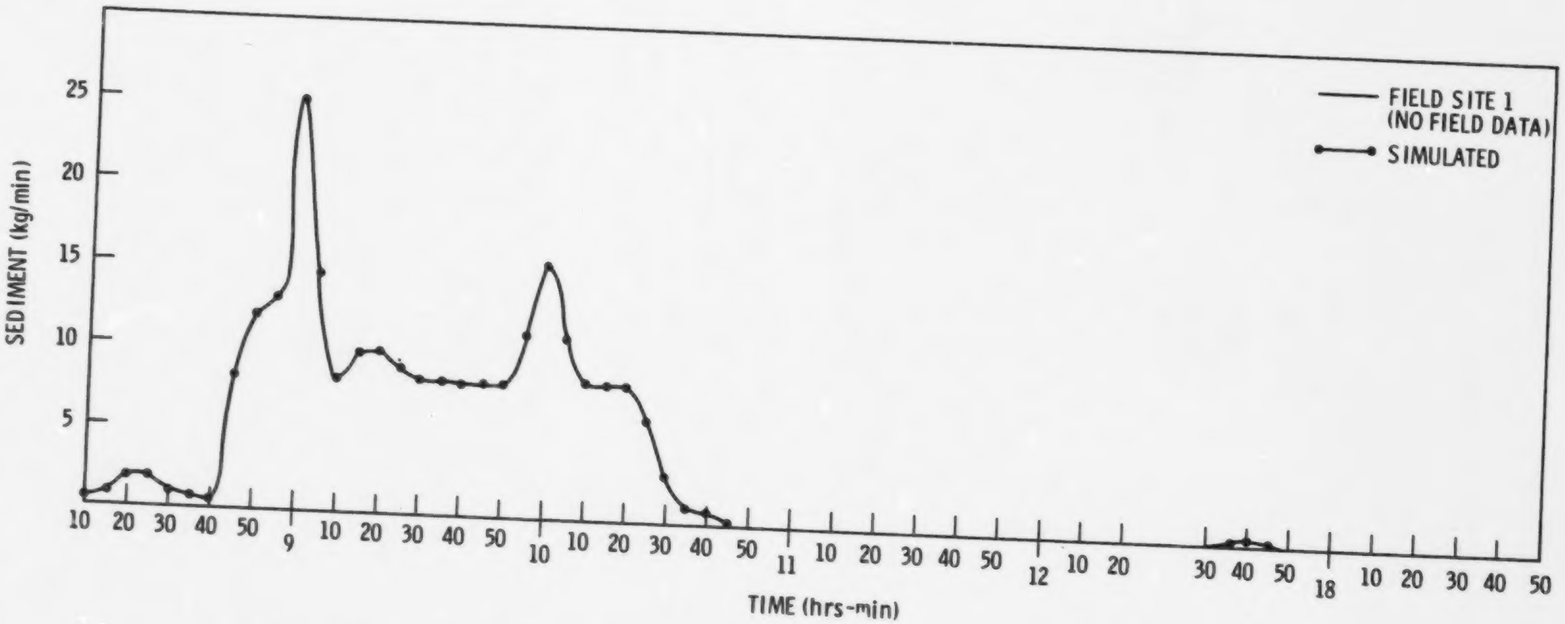


Figure 21. Simulated and measured sediment mass removal rate for the April 23, 1976 storm

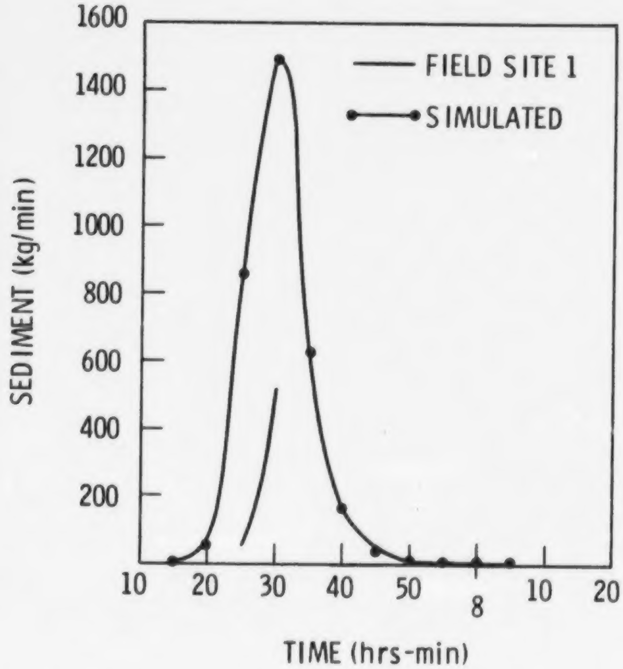


Figure 22. Simulated and measured sediment mass removal rate for the May 29, 1976 storm.

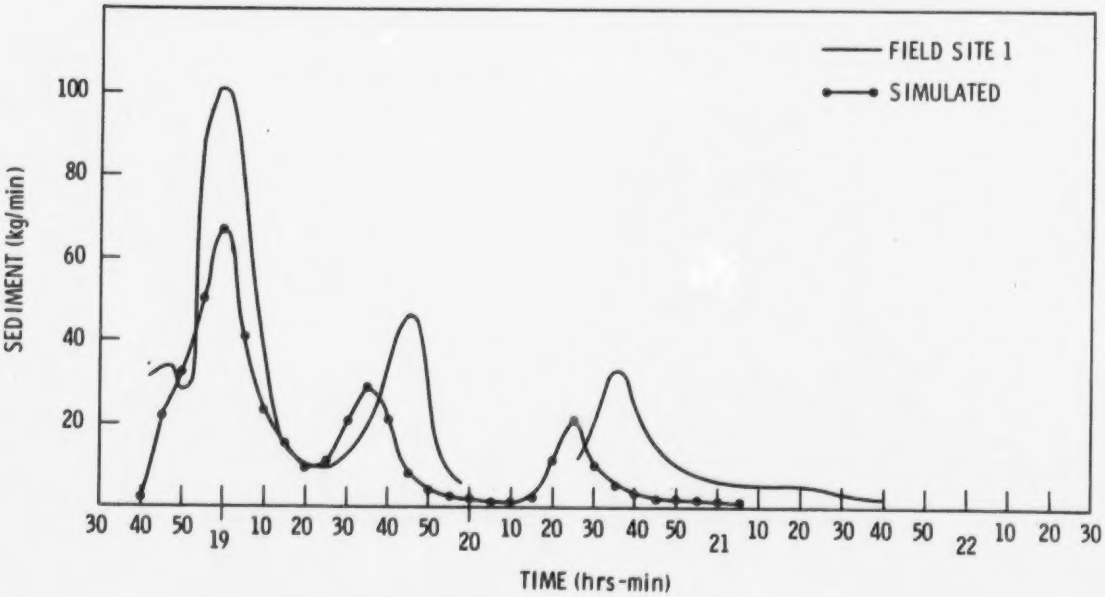


Figure 23. Simulated and measured sediment mass removal rate for the June 13, 1976 storm.

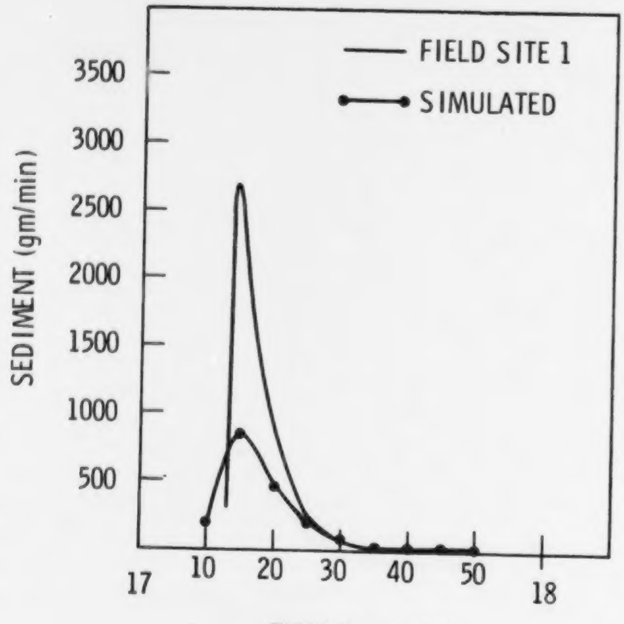


Figure 24. Simulated and measured sediment mass removal rate for the April 19, 1977 storm.

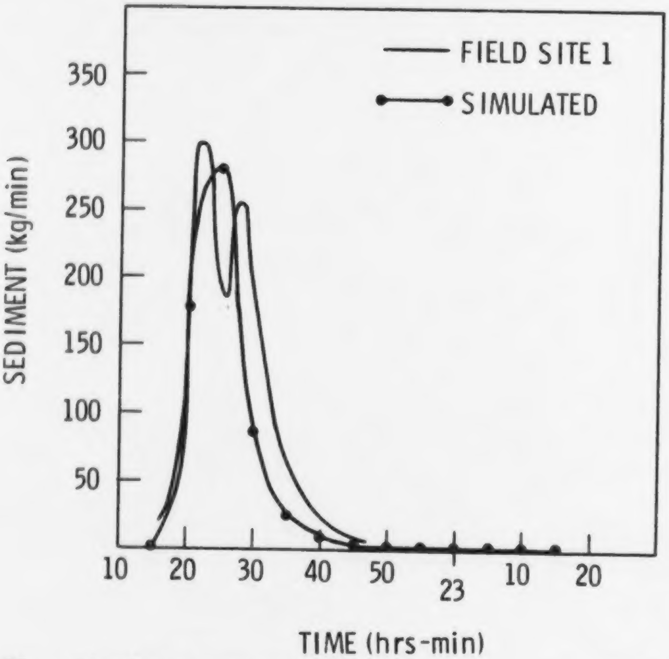


Figure 25. Simulated and measured sediment mass removal rate for the August 15, 1977 storm.

TABLE 7. COMPARISON OF SEDIMENT COEFFICIENTS

Coefficient	Battelle-Northwest	Leytham and Johanson(a)
JRER	2.2	2.2
KRER	0.25	0.43
JSER	2.2	1.8
KSER	1.8	0.9
SRERTL	2.0	2.0

(a) Average of values for Segments 1, 2 and 3

At the time of this study, data on pesticide concentrations in the runoff from Field Site 1 were limited. In addition, no data had been collected by ISU on the adsorption and desorption of alachlor on soils found in Four Mile Creek watershed. Data such as these are required to determine the coefficients for the Freundlich adsorption/desorption isotherm algorithm used in ARM. Recent experimental work on alachlor adsorption and desorption on a number of different soils provided values for the Freundlich isotherm coefficients (Jordan 1978). For soils of composition and organic matter content similar to the silt-loams commonly found in Four Mile Creek watershed, K and 1/N in the Freundlich adsorption/desorption isotherm alrogithm were found to be approximately 1.3 and 0.4, respectively. Since only limited pesticide runoff data were available, these coefficients were used without being tested. Future comparisons between simulated and measured pesticide runoff concentrations are required to verify the actual values of K and 1/N for alachlor at Four Mile Creek watershed.

Following the calibration of the hydrologic, sediment and pesticide coefficients, the ARM model was prepared for the test application. In order to obtain a long enough time history of pesticide concentrations for statistical analysis, a three-year simulation of runoff, sediment and pesticide contributions to Four Mile Creek was performed. Detailed meteorologic data from the ISU study, however, were not available for this duration. As a result, meteorological data collected at nearby weather stations were obtained from the National Climatic Center in Asheville, North Carolina. Table 8 lists each type of data required and the station from which it was obtained. The simulation time period selected was January 1970 through May 1974. The first year of data were used to calculate initial soil moisture and sediment conditions.

The dates for plowing, planting and cultivating were randomly selected within the approximate time periods given by Leytham and Johanson (1979) for each field operation (see Table 9). Soybeans were assumed to be the major crop planted in the study area and alachlor was applied to the soy-

TABLE 8. SOURCES OF METEOROLOGICAL DATA FOR THE TEST APPLICATION OF THE METHODOLOGY TO FOUR MILE CREEK WATERSHED

Date Type	Weather Station	Period of Record
Precipitation (hourly)	Traer, Iowa	August 1948 - December 1976
Pan Evaporation	Ames, Iowa	January 1962 - December 1973
Maximum and Minimum Air Temperature (daily)	Toledo, Iowa	April 1948 - December 1976
Wind Movement (daily)	Waterloo, Iowa	January 1961 - December 1976
Solar Radiation (daily)	Ames, Iowa	July 1959 - August 1972
Dewpoint Temperature (daily)	Waterloo, Iowa	January 1961 - December 1976

TABLE 9. APPROXIMATE TIME PERIODS FOR PLOWING, PLANTING AND CULTIVATING SOYBEANS AT FOUR MILE CREEK WATERSHED

Plowing	April 1 - May 1
Planting	May 5 - June 1
Cultivating	May 30 - July 1

beans the day after planting. The only constraint on the selection of a pesticide application date was that it could not occur on the same day as a storm event occurred.

In order to vary the rate of application of alachlor to the study area, it was assumed that conventional tillage practices, similar to those currently used on Four Mile Creek watershed, were used on the Gladbrook and southern catchments and that conservation tillage practices were used on the northern catchment. The application rate of alachlor on the conventionally tilled catchments was 1.8 kg/ha; this is the same application rate used on ISU Field Site 1 in 1976. Since the efficiency of weed control is usually reduced when conservation type practices were used, the alachlor application rate was increased to 2.3 kg/ha for the northern catchment.

Figures 26, 27, and 28 give a summary of the total simulated sediment and pesticide contributions from all three catchments during the study

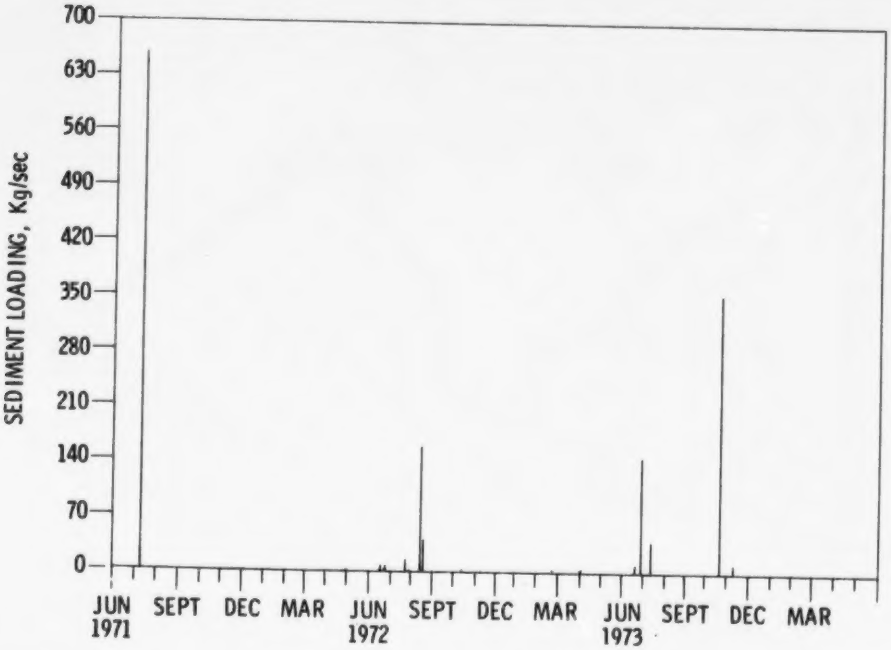


Figure 26. Time variation of predicted sediment loading to Four Mile Creek during the three year simulation period

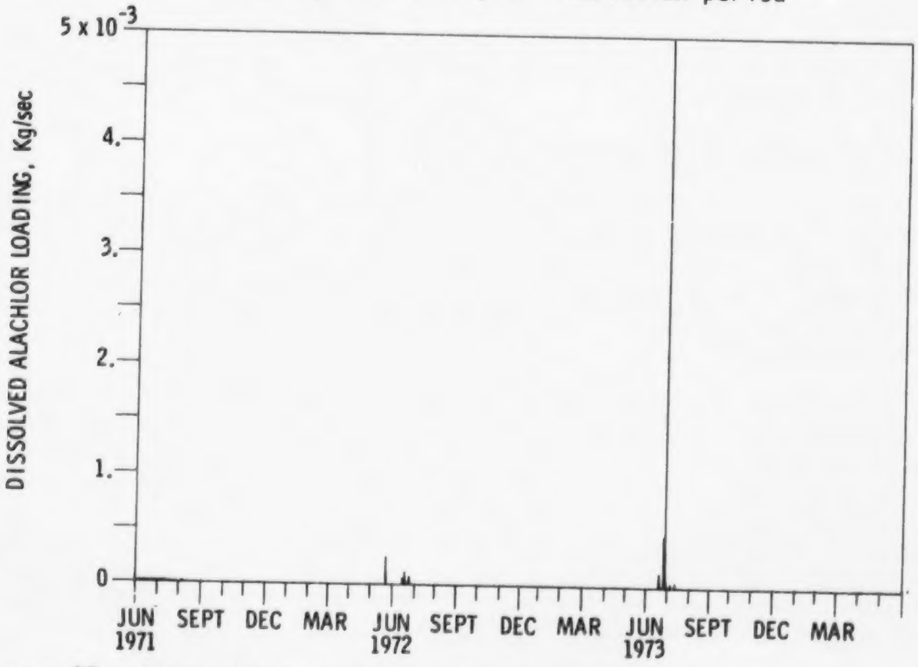


Figure 27. Time variation of predicted dissolved alachlor loading to Four mile creek during the three year simulation period

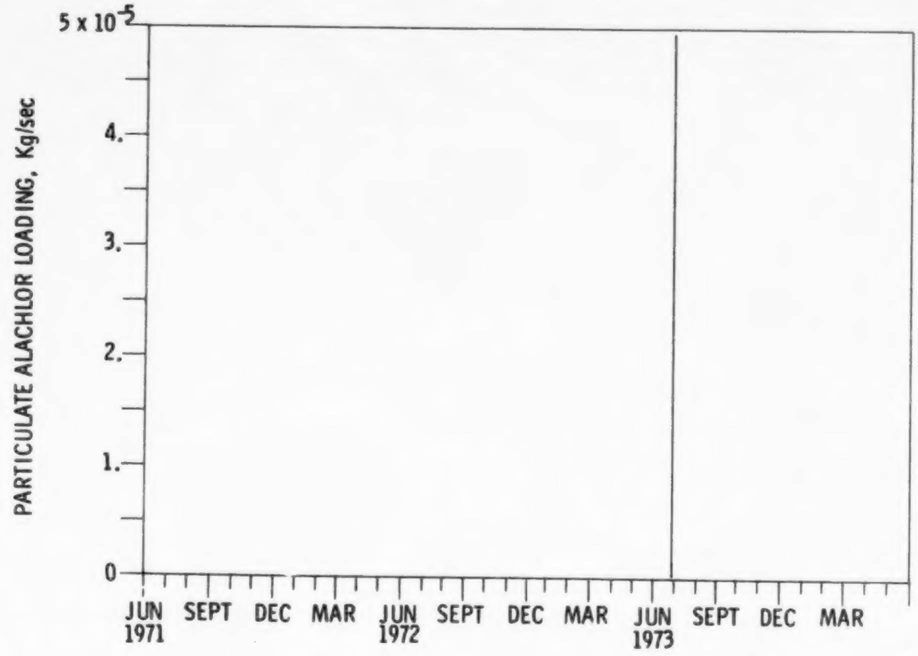


Figure 28. Time variation of predicted particulate alachlor loading to to Four Mile Creek during the three year simulation period

period. Simulation results show that the major runoff events at Four Mile Creek watershed occur between May and September each year but not in winters or early spring.

INSTREAM PESTICIDE MODELING

As shown in Figure 15, the study area for the instream modeling was a 67.6 km reach between River Kilometer 19.3 in Four Mile Creek and the mouth of Wolf Creek. Four Mile Creek joins Wolf Creek at River Kilometer 48.3 of Wolf Creek. Runoff, sediment loading and pesticide loading from the three catchments calculated by the ARM model were introduced to Four Mile Creek at River Kilometer 9.7.

Unlike the overland pesticide modeling discussed above, almost no measured data were available for the instream pesticide modeling. Discharge measurements of Four Mile Creek conducted at Traer (River Kilometer 4.2) during the three year simulation period indicate the large variation of daily discharge ranging from 9.65 m^3/sec to 0.006 m^3/sec. The average discharge at Traer during this period was 0.46 m^3/sec. Since the purpose of the methodology application to Four Mile and Wolf Creeks was to evaluate the CMRA Methodology and not to perform an assessment in this area, actual flow variations were simplified for this study.

The base flows of Four Mile and Wolf Creeks without runoff contributions was assumed to be 2 m^3/sec and 7 m^3/sec, respectively. Test conditions for the instream modeling are shown in Table 10. Based on field data obtained by ISU (Baker et al. 1979), it was assumed that the river sediment consists of 65% sand, 15% silt and 20% clay. For eroded soil from the overland, Baker et al. (1979) show a variation in a particle size distribution as a function of time and sediment concentration for the 4/19/77 runoff event which occurred at Field Site 1. Based on these particle size distribution analyses performed by ISU on a selected runoff sampler, calculated total sediment loading from these three catchments were assumed to consist of 0% sand, 40% silt and 60% clay. Particle sizes of sand, silt and clay were assumed to be 0.350 mm, 0.01 mm, and 0.0014 mm, respectively. No field or laboratory studies were performed to evaluate critical shear stresses (τ_{CRj} and τ_{CDj}) and the erodibility coefficient (M_j), needed to calculate erosion and deposition of cohesive sediments (see detailed model formulations of SERATRA in Onishi and Wise 1979c). These parameters were determined through a trial and error calibration procedure. The bed shear stresses at each location for each time step were calculated by SERATRA code internally with a known hydraulic condition.

The distribution coefficient, Kd, of alachlor associated with the bulk sediment was estimated to be 50 ml/g in receiving streams (Baker et al. 1979). In this study, Kd values of alachlor with sand, silt and clay were rather arbitrarily assumed to be 2, 20, and 100 ml/g. The total pesticide alachlor for each storm event was then distributed to each sediment size fraction as follows: A ratio of the selected Kd values of sand to those of silt and clay is 1:10:50. Hence for an equal amount of sand, silt and clay, clay contains five times more alachlor than silt, which in turn contains 10 times more alachlor than sand. Since the sediment loading from overland was assumed to be 40% silt and 60% clay, total particulate alachlor contributed from the three catchments was divided into 0, 12 and 88% each associated with eroded overland sand, silt and clay, respectively at the stream edge. Because of the lack of available data, the transfer rate, K_j, for alachlor to moving sediment and stationary bed sediment to reach to an equilibrium condition assigned by a distribution coefficient were arbitrarily assigned values of 0.36 and 0.01 per hour, respectively. Although SERATRA simulates various chemical and biological degradation of dissolved pesticides individually, there were no available data to enable the simulation of degradation by each process. Hence in this study, all pesticide degradation was lumped into a first order reaction having a degradation rate of 0.003 per hour. This rate was estimated from preliminary information supplied by Monsanto Agricultural Product Co.

Simulation of sediment and alachlor transport was conducted for each of the following substances: 1) sand, 2) silt, 3) clay, 4) dissolved alachlor, 5) particulate alachlor associated with sand, 6) particulate alachlor attached to silt, and 7) particulate alachlor adsorbed by clay. The modeling procedure for SERATRA involved simulating sediment transport of sand, silt and clay. The results were then used to simulate dissolved and particulate alachlor by including the effects of alachlor-sediment interaction. Finally, changes in stream bed conditions were recorded, including: 1) stream bed elevation change, 2) vertical and longitudinal distributions of ratios of sand, silt and clay within the bed, and 3) vertical and longitudinal distributions of alachlor within the stream bed. A

TABLE 10. TEST CONDITIONS FOR SEDIMENT AND PESTICIDE TRANSPORT MODELING

Base Flow, m^3/sec	
Four Mile Creek	2
Wolf Creek	7
Manning Coefficient	
Four Mile Creek	0.07
Wolf Creek	0.04
Sediment Sizes, mm	
Sand	0.35
Silt	0.016
Clay	0.0014
Bed Sediment Size Fraction, %	
Sand	65
Silt	15
Clay	20
Size Fraction of Eroded Sediment from Overland, %	
Sand	0
Silt	40
Clay	60
Erodibility Coefficient, kg/m^3	
Four Mile Creek	
Silt	1×10^{-4}
Clay	1×10^{-4}
Wolf Creek	
Silt	1×10^{-4}
Clay	1×10^{-4}
Critical Shear Stress for Erosion, kg/m^2	
Four Mile Creek	
Silt	1.5
Clay	1.7
Wolf Creek	
Silt	0.55
Clay	0.6
Critical Shear Stress for Deposition, kg/m^2	
Four Mile Creek	
Silt	0.7
Clay	0.6
Wolf Creek	
Silt	0.4
Clay	0.3
Vertical Diffusion Coefficient, m^2/sec	1×10^{-6}
Distribution Coefficient, m^3/kg	
With Sand	0.002
Silt	0.020
Clay	0.10
Transfer Rate, 1/hr	
Moving Sediment	0.36
Non-moving Sediment	0.001
Total Alachlor Degradation, 1/hr	0.003

brief discussion of the simulation results will be presented here. More detailed instream simulation results as well as mathematical formulation of SERATRA were reported by Onishi and Wise (1979c).

Calibrations of EXPLORE-I to obtain proper depth and velocity distributions in Four Mile and Wolf Creeks were performed using the predicted largest runoff event (by ARM) which occurred during the three-year simulation period. This event resulted in the maximum discharge of 18.1 m^3/sec in Four Mile Creek. The duration of the calibration run was 10 days starting from July 8 to July 17, 1971. After numerous trial runs, the proper Manning coefficients in Four Mile and Wolf Creeks were determined to be 0.07 and 0.04, respectively. These Manning coefficient values were judged reasonable for these small streams.

After ensuring mass conservation, EXPLORE-I and ARM simulation results were input to SERATRA for the model calibration. The only parameters and coefficients that require adjustment are the vertical dispersion coefficient and the three parameters, i.e., erodibility coefficient, M_j and critical shear stresses for erosion deposition, τ_{CRj} and τ_{CDj} used to calculate deposition and erosion rates of cohesive sediments. Transport of noncohesive sediments (sand) does not require the model calibration. The other parameters (e.g., pesticide distribution coefficients and degradation rate, sediment sizes, etc) are determined by theoretical and experimental analyses and field conditions prior to the model simulation. Thus most of the calibration effort was oriented toward reproducing sediment distribution patterns similar to the actual or estimated longitudinal and vertical distributions of sediment concentrations for the 67.6-km study reach. For model calibration, Four Mile and Wolf Creeks were divided into fourteen 4.83-km segments. A fifteen minute time step was used. After trial and error, the values shown in Table 10 were selected for these sediment erosion and deposition parameters.

Time variations of computed sediment concentration for each sediment size fraction and the sum of the three size fractions near the mouth of Four Mile Creek (River Kilometer 2.5) are shown in Figure 29. This figure indicates that the majority of sediment is clay. Figure 30 shows time variations of computed particulate alachlor associated with each sediment size fraction, together with mean particulate alachlor concentrations (weighted average of three particulate alachlor concentrations associated with sand, silt and clay) near the mouth. Because clay has the largest Kd value, the particulate pesticide concentration associated with clay has the highest concentration. Sand contains the lowest pesticide concentration. Variations of computed dissolved, particulate and total (sum of dissolved and particulate pesticide concentrations) alachlor concentrations with time near the Four Mile Creek mouth are shown in Figure 31. The figure reveals that more than 75% of alachlor near the mouth of Four Mile Creek was transported in the dissolved form and that up to 25% of alachlor was carried by sediment. This implies that sediment transport becomes important when a pesticide has a large distribution coefficient, Kd, or a receiving water body contains very high sediment concentrations.

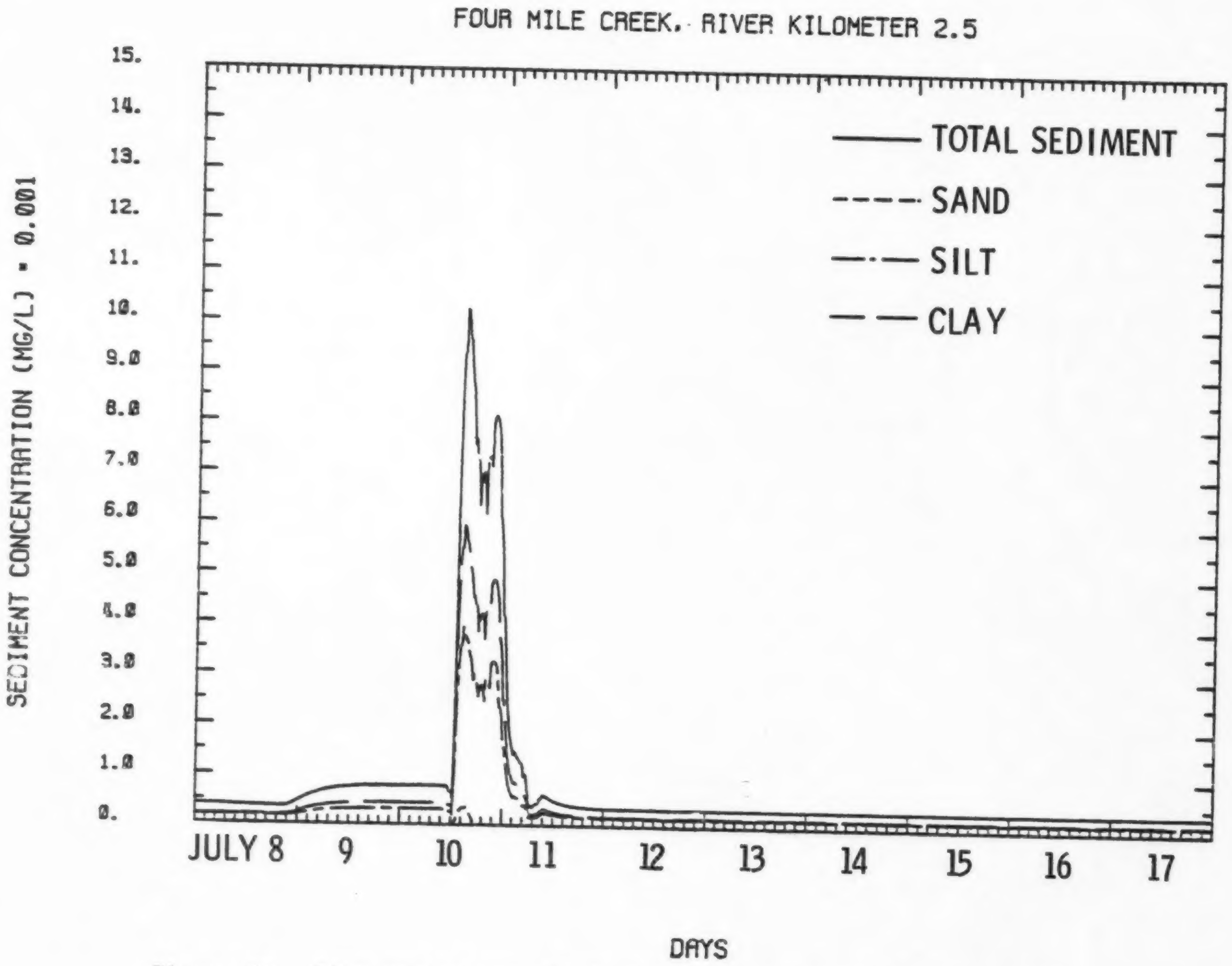


Figure 29. Time variations of simulated concentration of sand, silt, clay and total sediment at Four Mile Creek River Kilometer 2.5.

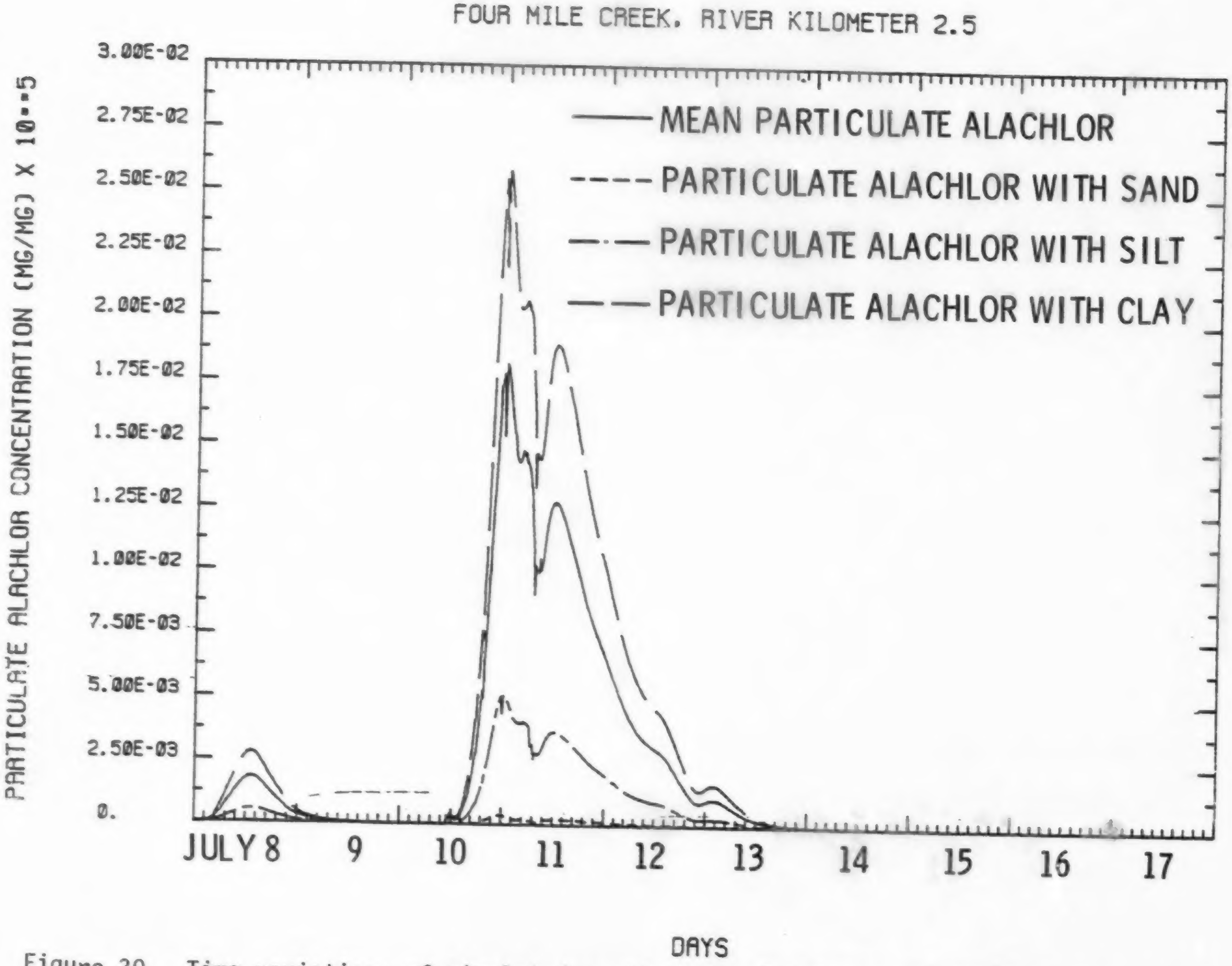


Figure 30. Time variations of simulated particulate alachlor concentrations associated with sand, silt and clay, together with mean particulate alachlor concentrations at Four Mile Creek River Kilometer 2.5.

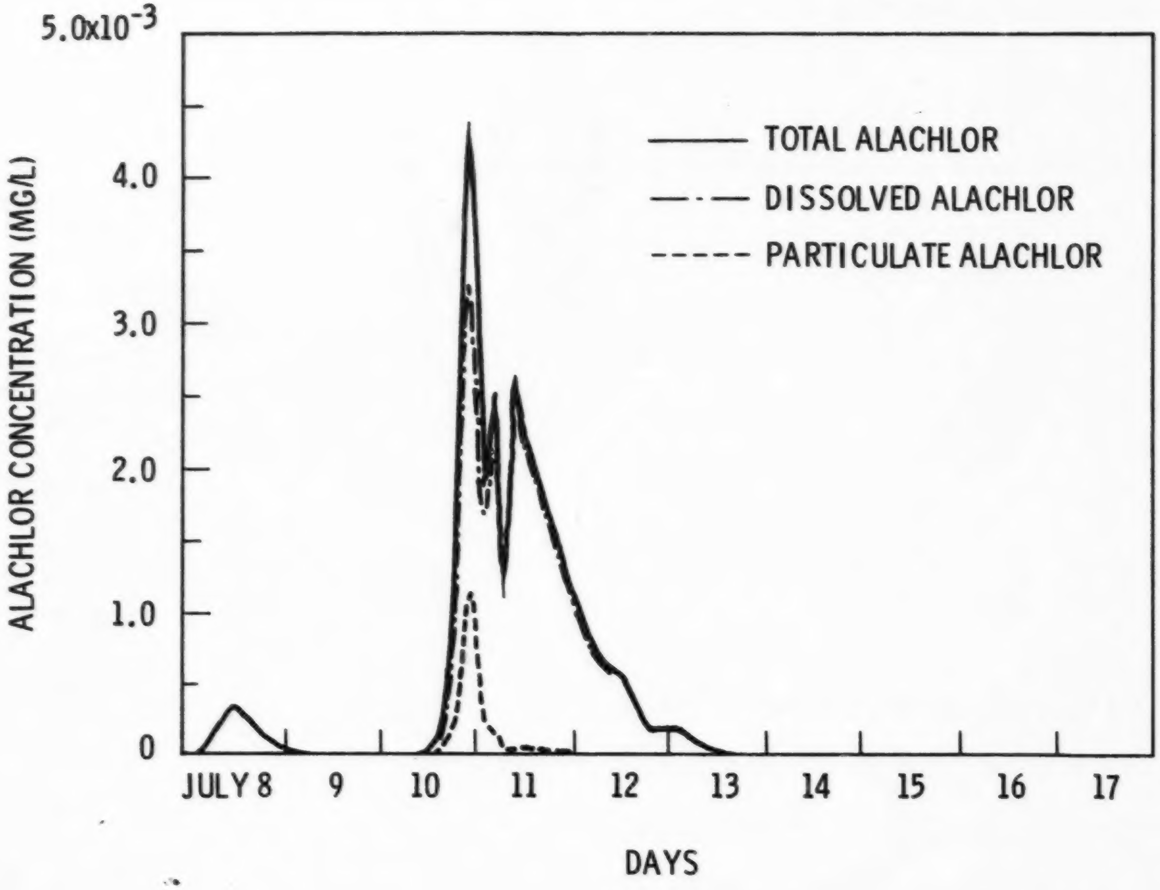


Figure 31. Time variations of simulated dissolved, particulate and total alachlor concentrations at Four Mile Creek River Kilometer 2.5

Vertical distributions of sediment and alachlor concentrations near the mouth of Four Mile Creek are shown in Figures 32, 33 and 34. In these figures, elevations of water and bed surfaces are 272.56 m and 271.77 m, respectively. Figure 32 indicates that all suspended sediments have higher concentrations near the river bed, but cohesive sediments show relatively more uniform vertical distributions. This is due to the smaller fall velocities of silt and clay as compared to the fall velocity of sand. Figure 33 presents vertical distributions of particulate alachlor concentrations per unit weight of sand, silt and clay. This figure reveals that except those attached to sand, particulate alachlor concentrations are almost vertically uniform. Vertical distributions of average particulate (weighted average of particulate alachlor associated with sand, silt and clay), dissolved and total alachlor concentrations are shown in Figure 34. In this figure, dissolved alachlor concentration is also shown to be almost vertically uniform. However, the particulate alachlor concentration per unit volume of water indicates higher concentration near the river bed due to higher sediment concentrations near the bed. The total alachlor concentration (sum of dissolved and particulate alachlor concentrations) reflects patterns of dissolved and particulate alachlor distributions.

Following model calibration, EXPLORE-I and SERATRA were used to simulate pesticide migration for the three-year duration between June 1971 and May 1974. For this case, the entire study reach was divided into seven equal-distance segments and a 30 minute time step was used to reduce the required computational time. Some of the simulation results near the mouth of Wolf Creek (River Kilometer 5) are shown in Figures 35 through 46. Figure 35 shows the time variation of flow rate calculated near the mouth of the Wolf Creek. The figure indicates that all 10 high flows occurred during the three-year simulation period happened to occur in summer and fall. Snow melt did not produce significant runoff to receiving waters.

Time variation of total sediment concentration near the Wolf Creek mouth is shown in Figure 36, which clearly indicates a small number of sharp peaks associated with high flows shown in Figure 35.

Figures 37 and 38 indicate time variations of total particulate pesticide concentrations associated with sediments per unit weight of sediment and per unit volume of water, respectively. There are two large peaks of particulate alachlor concentrations per unit weight of sediment (Figure 37) but only one large peak of particulate pesticide concentrations per unit volume of water (Figure 38). This is due to the fact that although alachlor concentrations attached to sediment per unit weight of sediment during the summer of 1972 is high, the sediment concentration during the same period is relatively low, so that the particulate alachlor concentration per unit volume of water becomes low.

Dissolved and total (sum of dissolved and particulate) alachlor concentrations near the mouth of Wolf Creek are shown in Figures 39 and 40, respectively. There are two high peaks of dissolved and total alachlor during the three-year simulation period. Figures 35 through 40 clearly

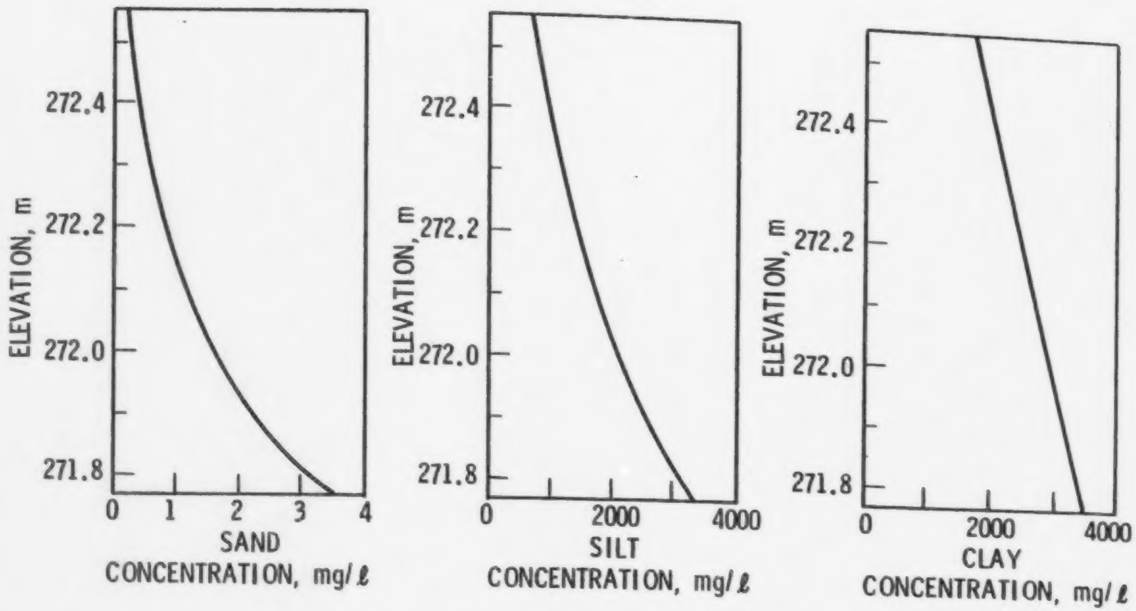


Figure 32. Vertical distributions of simulated sediment concentrations at Four Mile Creek River Kilometer 2.5 at 12:00 p.m., July 10, 1971.

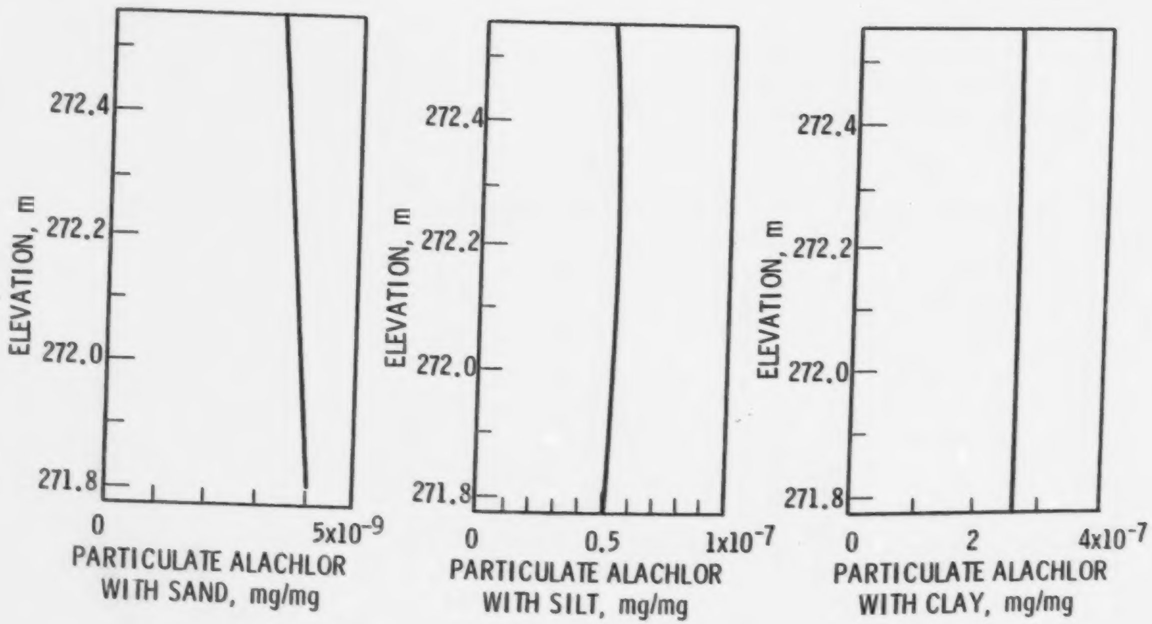


Figure 33. Vertical distributions of simulated particulate alachlor adsorbed by sediments at Four Mile Creek River Kilometer 2.5 at 12:00 p.m., July 10, 1971.

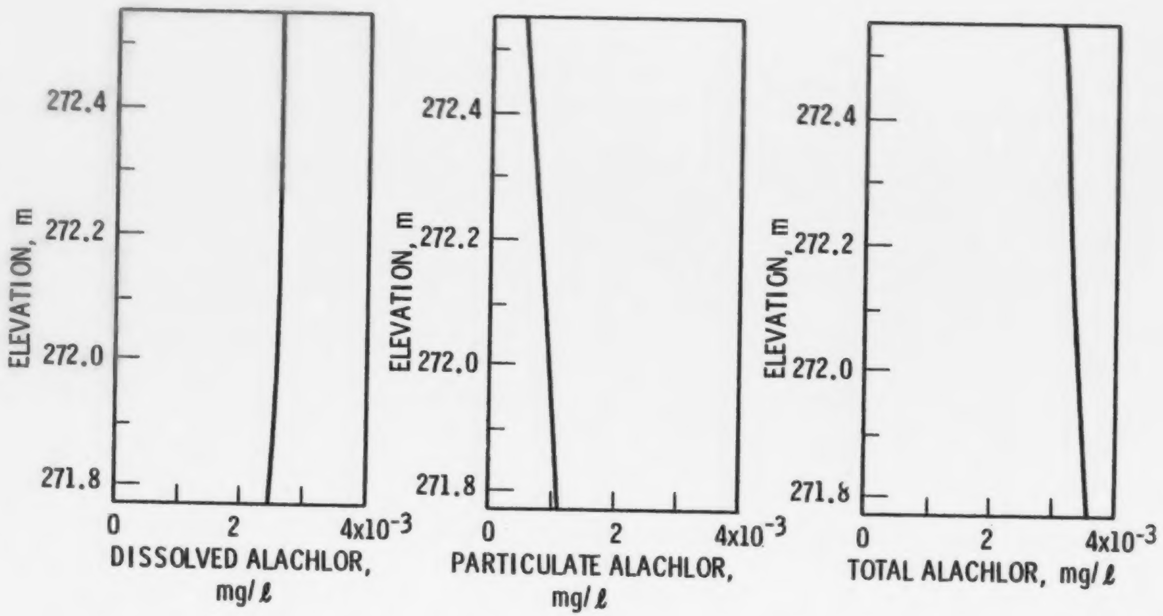


Figure 34. Vertical distributions of simulated dissolved, particulate and total alachlor concentrations at Four Mile Creek River Kilometer 2.5 at 12:00 p.m., July 10, 1971.

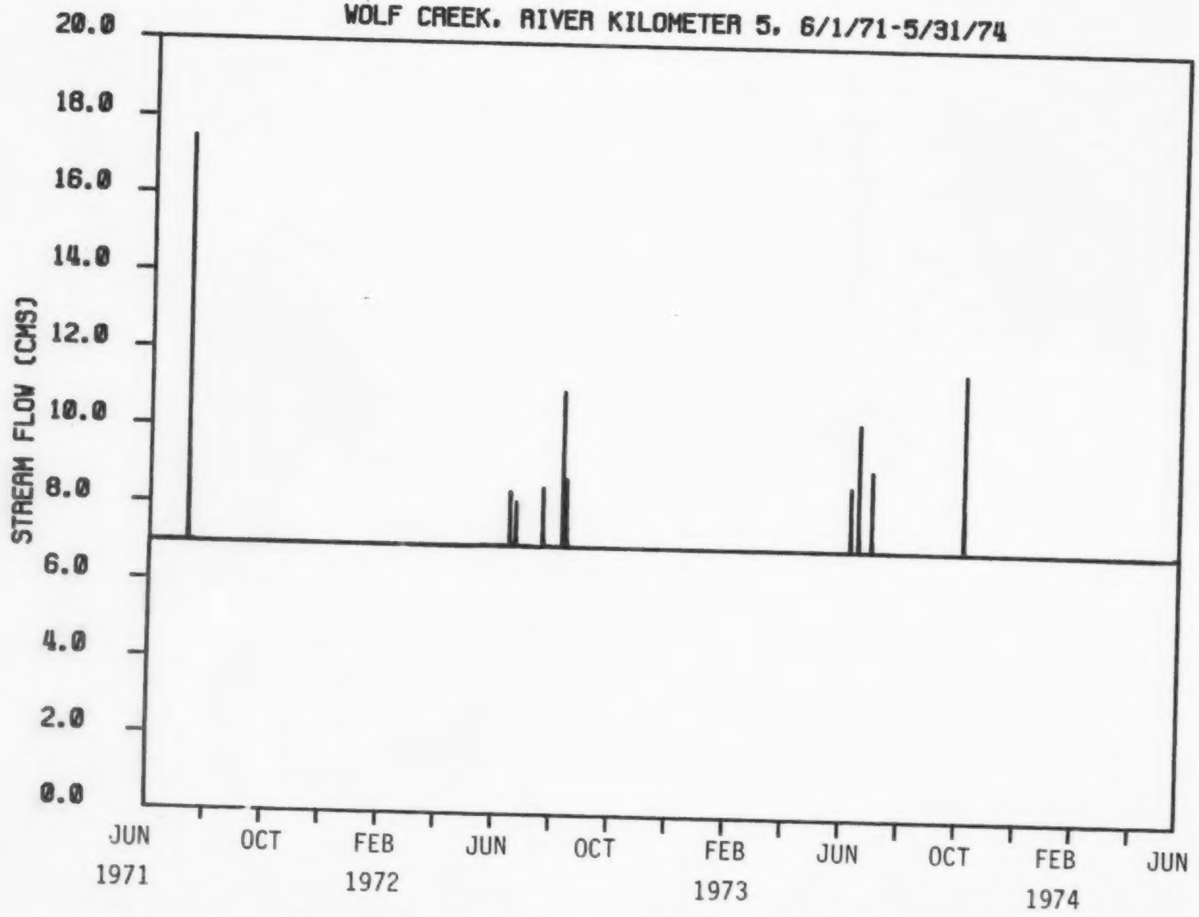


Figure 35. Time variation of predicted flow rate at Wolf Creek River Kilometer 5 during the three-year simulation period.

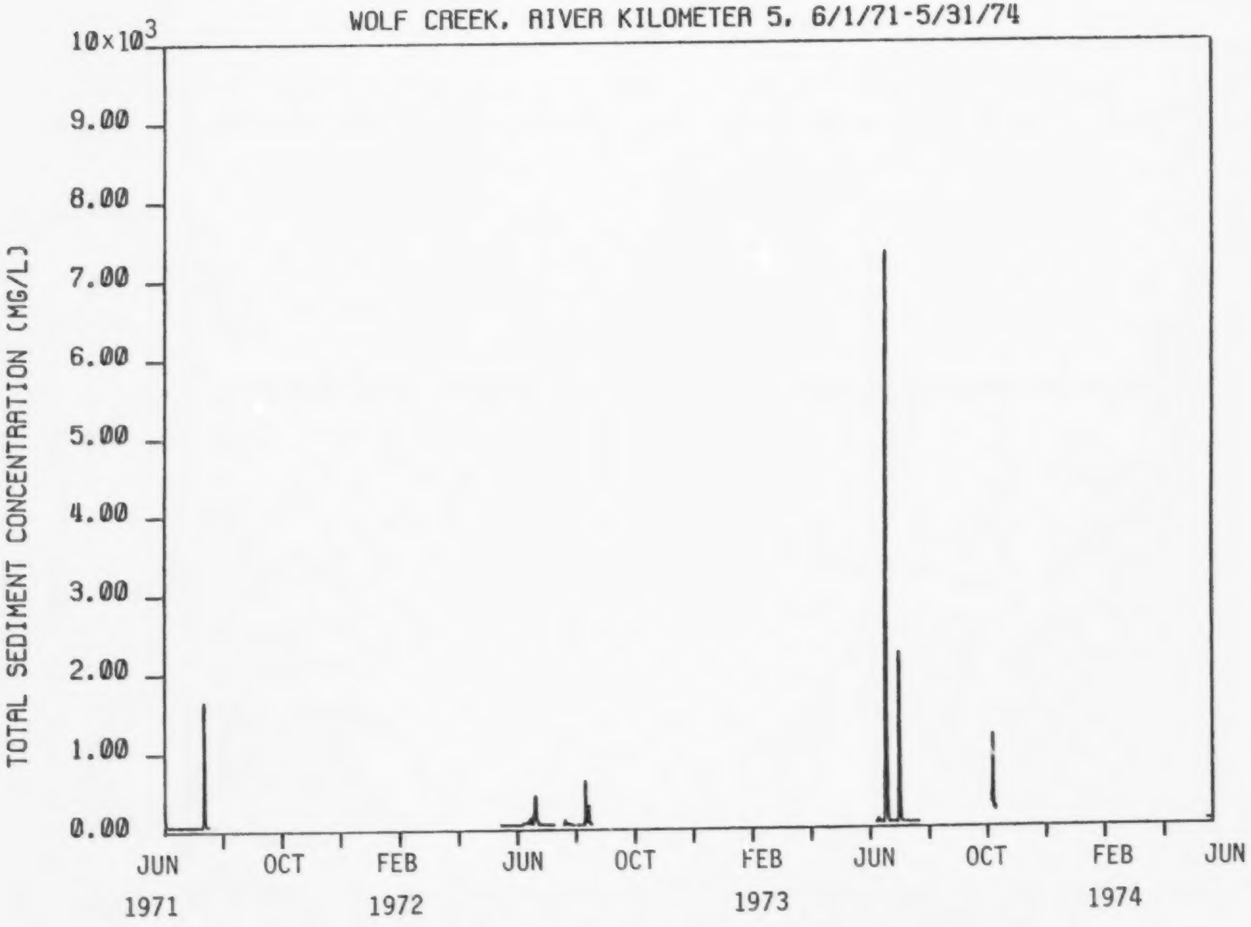


Figure 36. Time variation of predicted total sediment concentration at Wolf Creek River Kilometer 5 during the three-year simulation period.

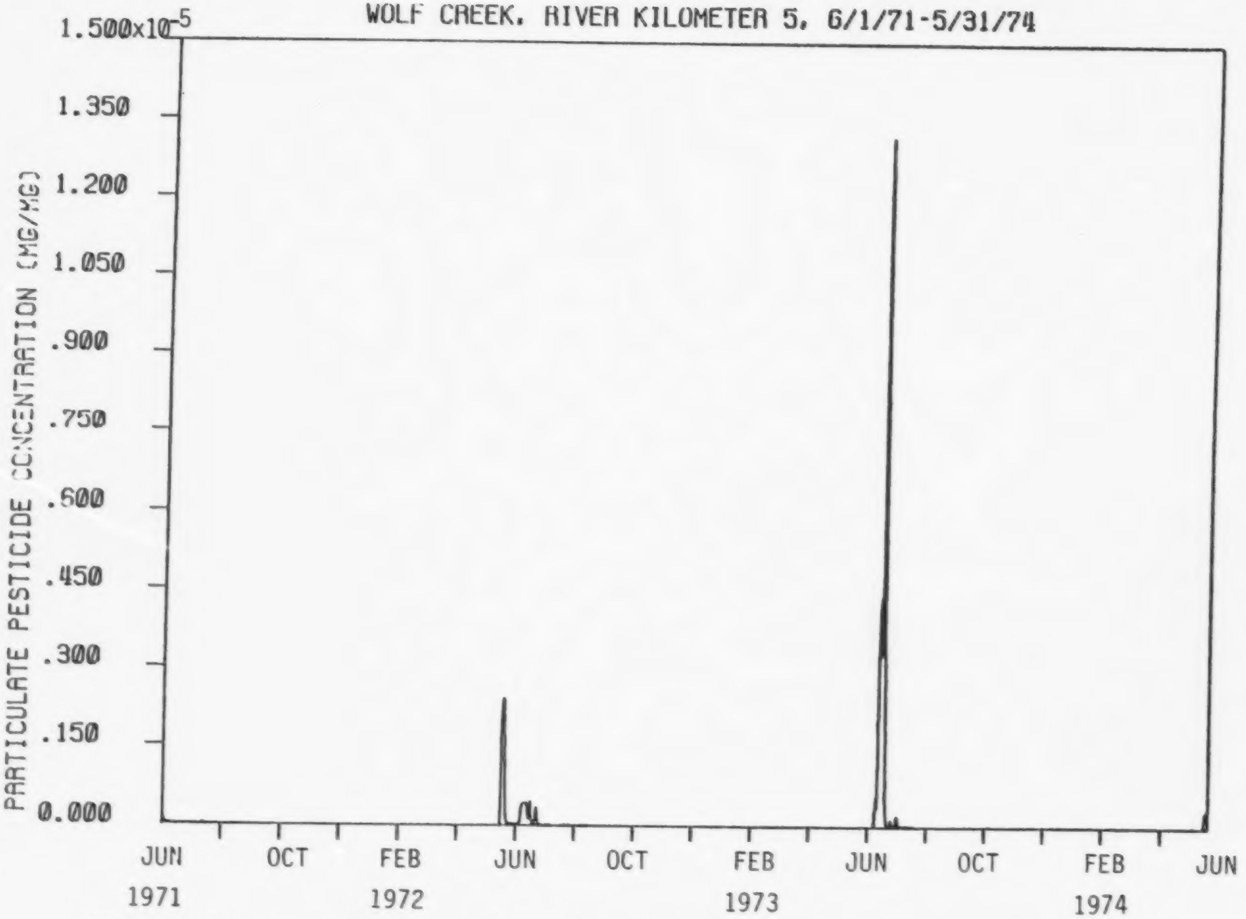


Figure 37. Time variation of predicted particulate alachlor concentration per unit weight of sediment at Wolf Creek River Kilometer 5 during the three-year simulation period.

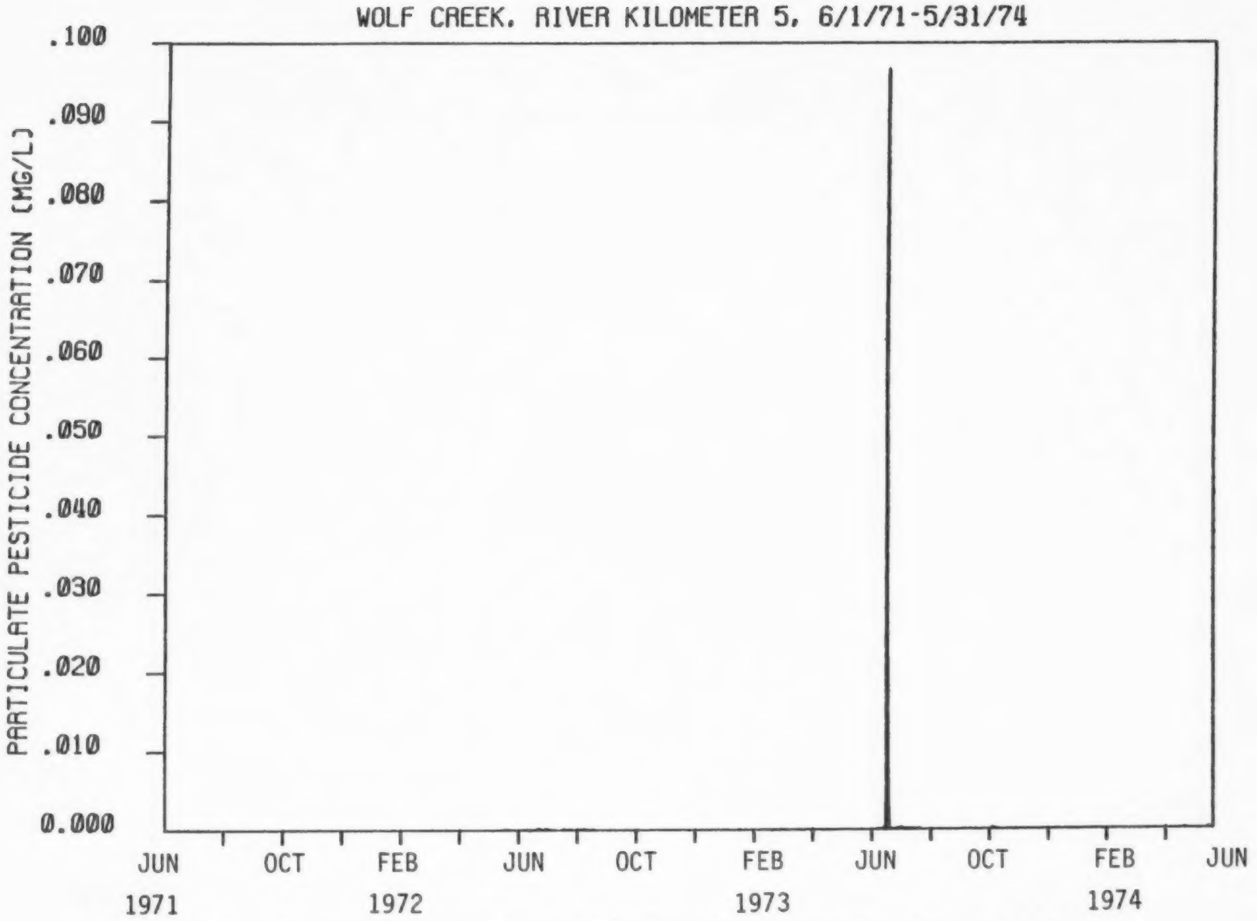


Figure 38. Time variation of predicted particulate alachlor concentration per unit volume of water at Wolf Creek River Kilometer 5 during the three-year simulation period.

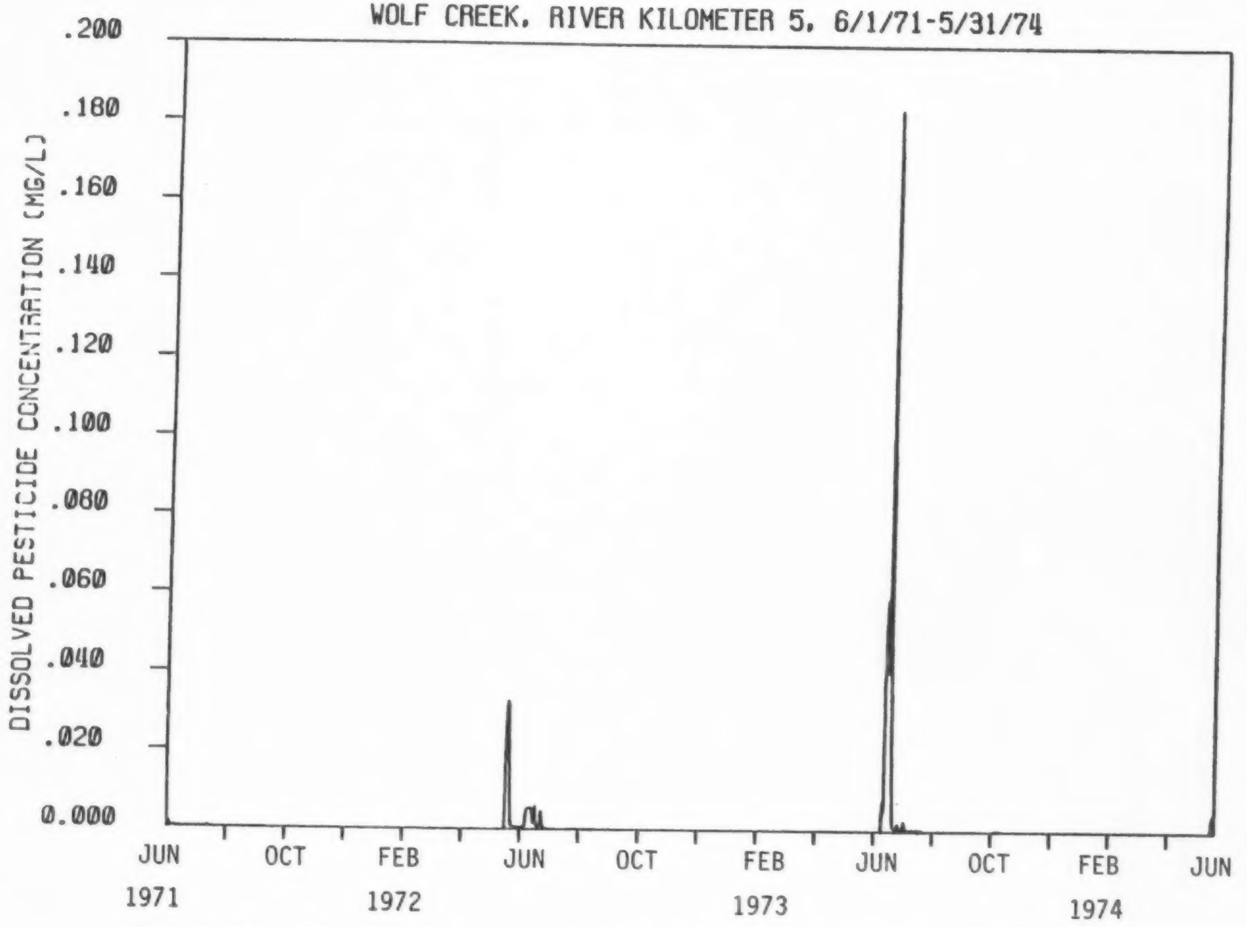


Figure 39. Time variation of predicted dissolved alachlor concentration at Wolf Creek River Kilometer 5 during the three-year simulation period.

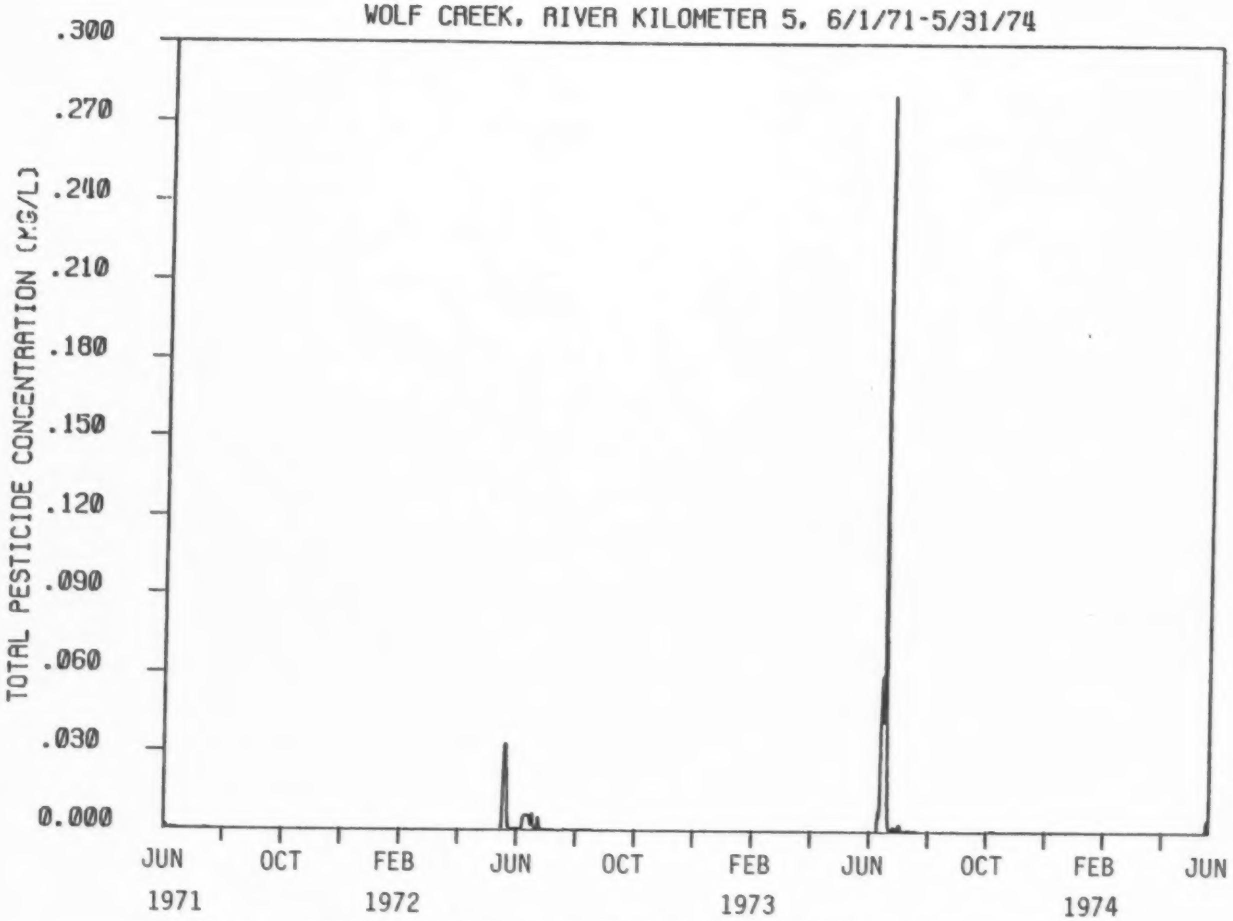


Figure 40. Time variation of predicted total alachlor concentration at Wolf Creek River Kilometer 5 during the three-year simulation period.

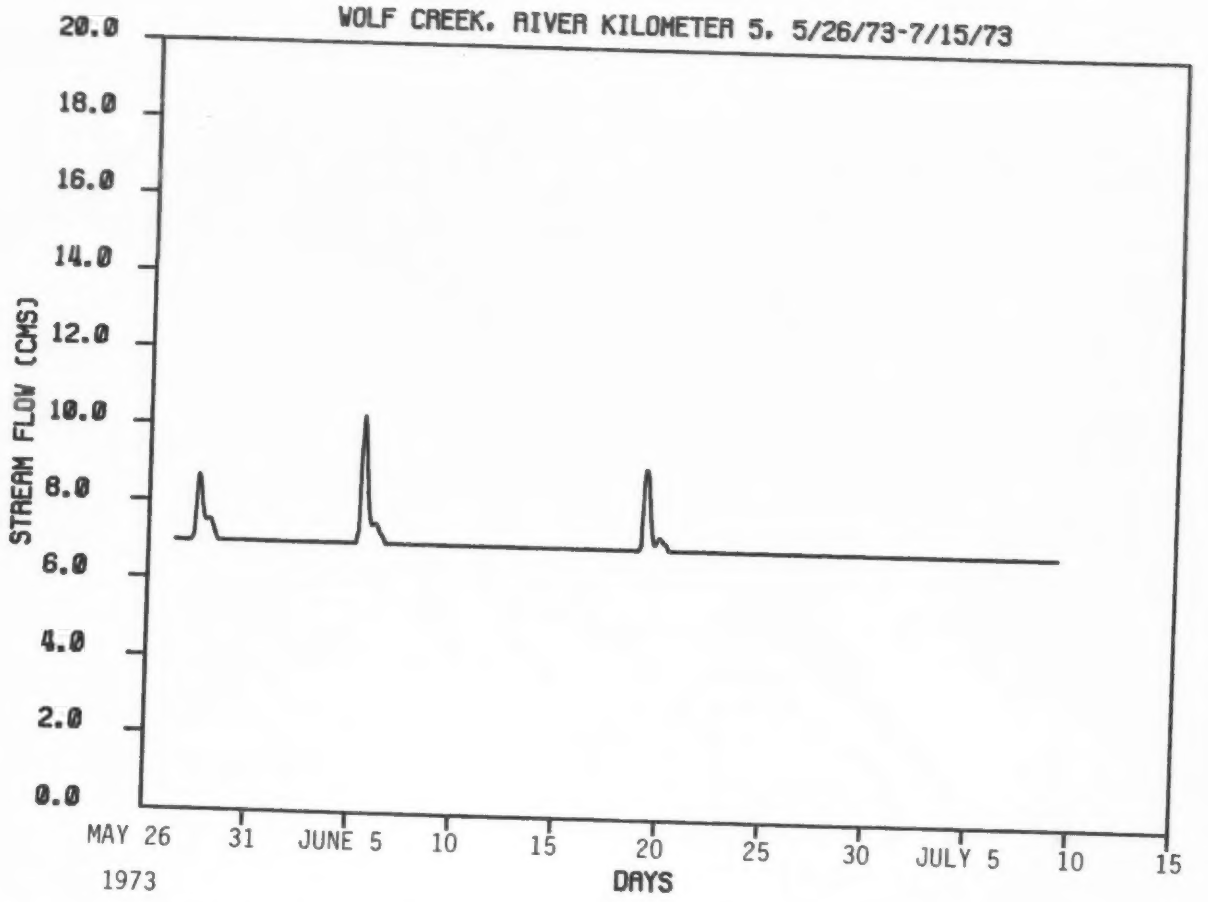


Figure 41. Time variation of simulated flow rate at Wolf Creek River Kilometer 5 during May 26, 1973 to July 15, 1973.

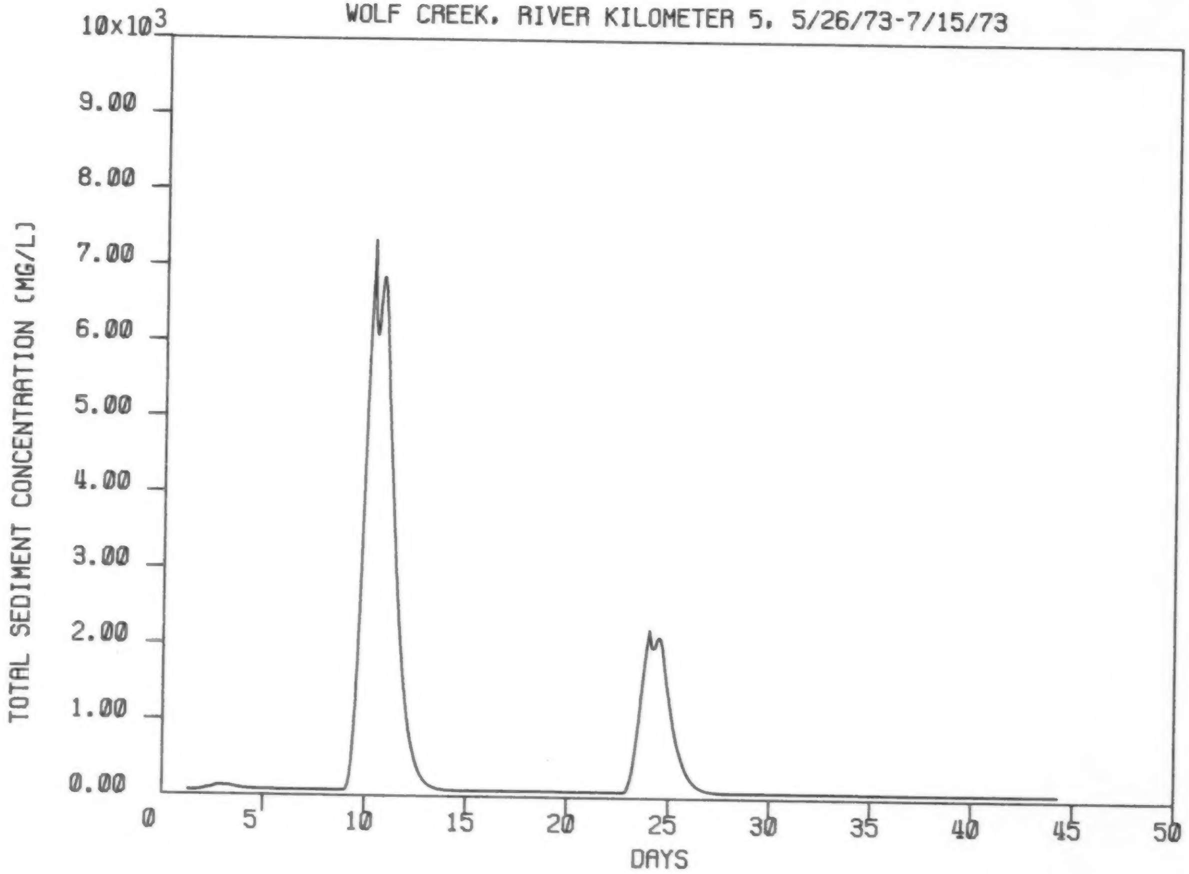


Figure 42. Time variation of simulated total sediment concentration at Wolf Creek River Kilometer 5 during May 26, 1973 to July 15, 1973.

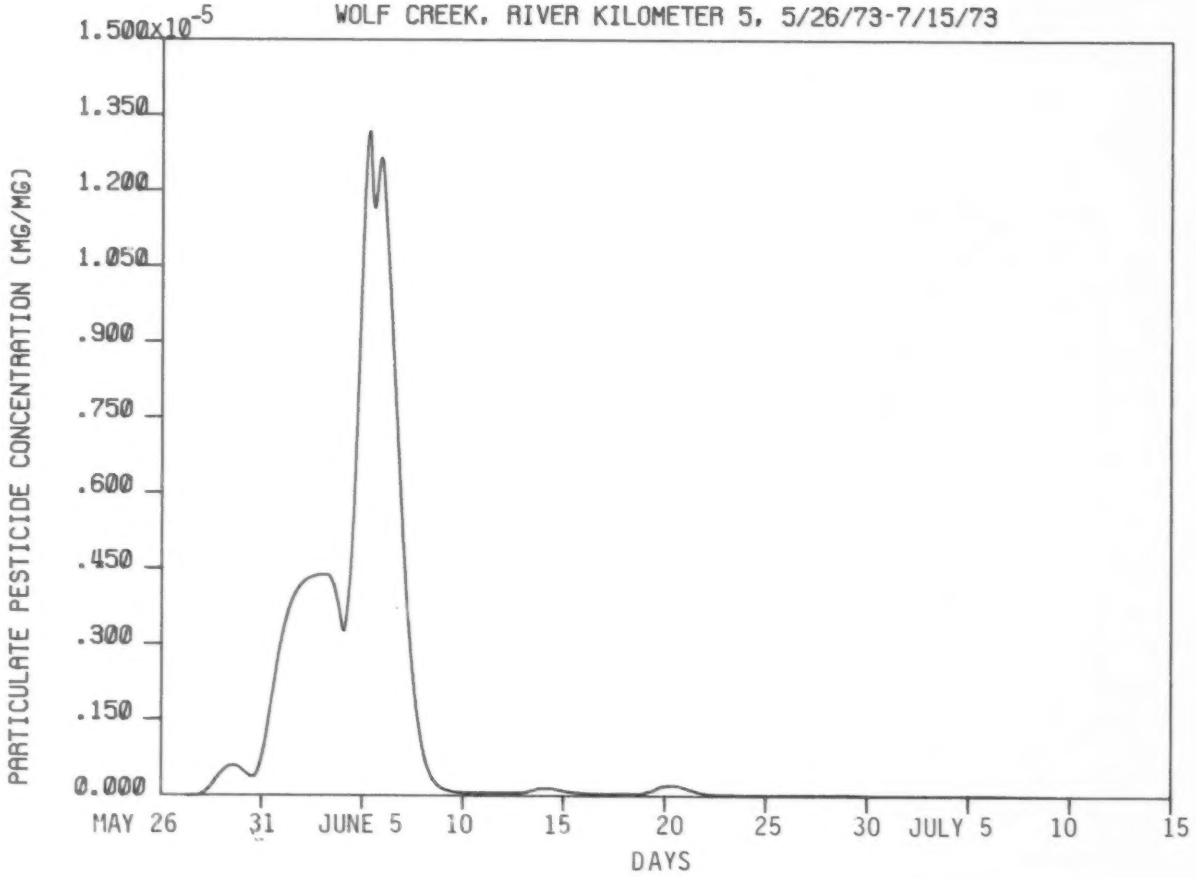


Figure 43. Time variation of simulated particulate alachlor concentration at Wolf Creek River Kilometer 5 during May 26, 1973 to July 15, 1973.

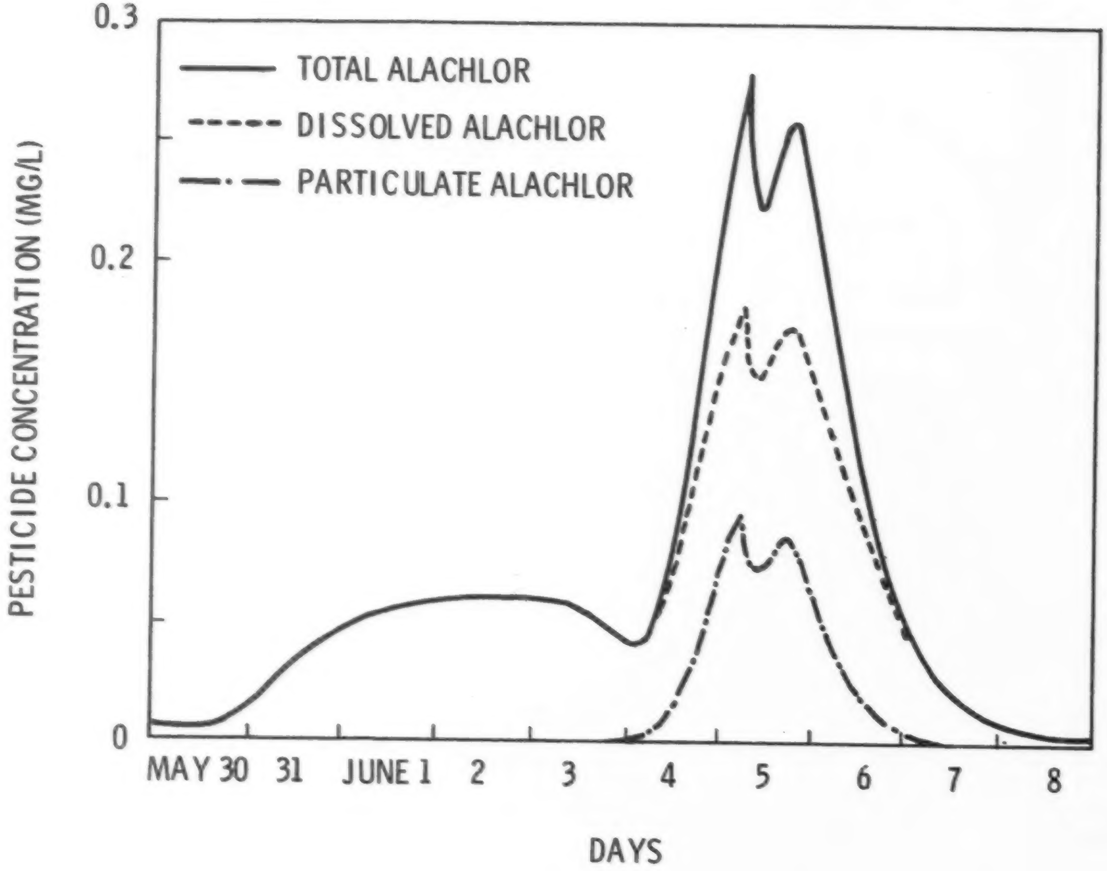


Figure 44. Time variation of simulated dissolved, particulate and total alachlor concentrations at Wolf Creek River Kilometer 5 during May 30, 1973 to June 9, 1973.

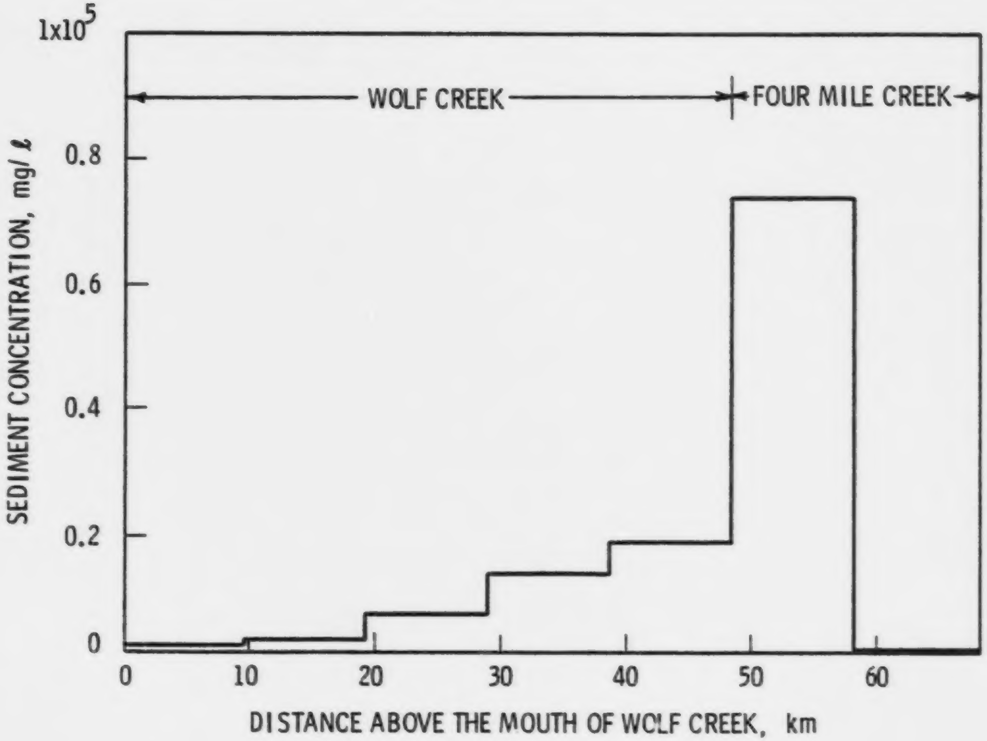


Figure 45. Longitudinal distribution of simulated total sediment concentration at 6 a.m., June 4, 1973.

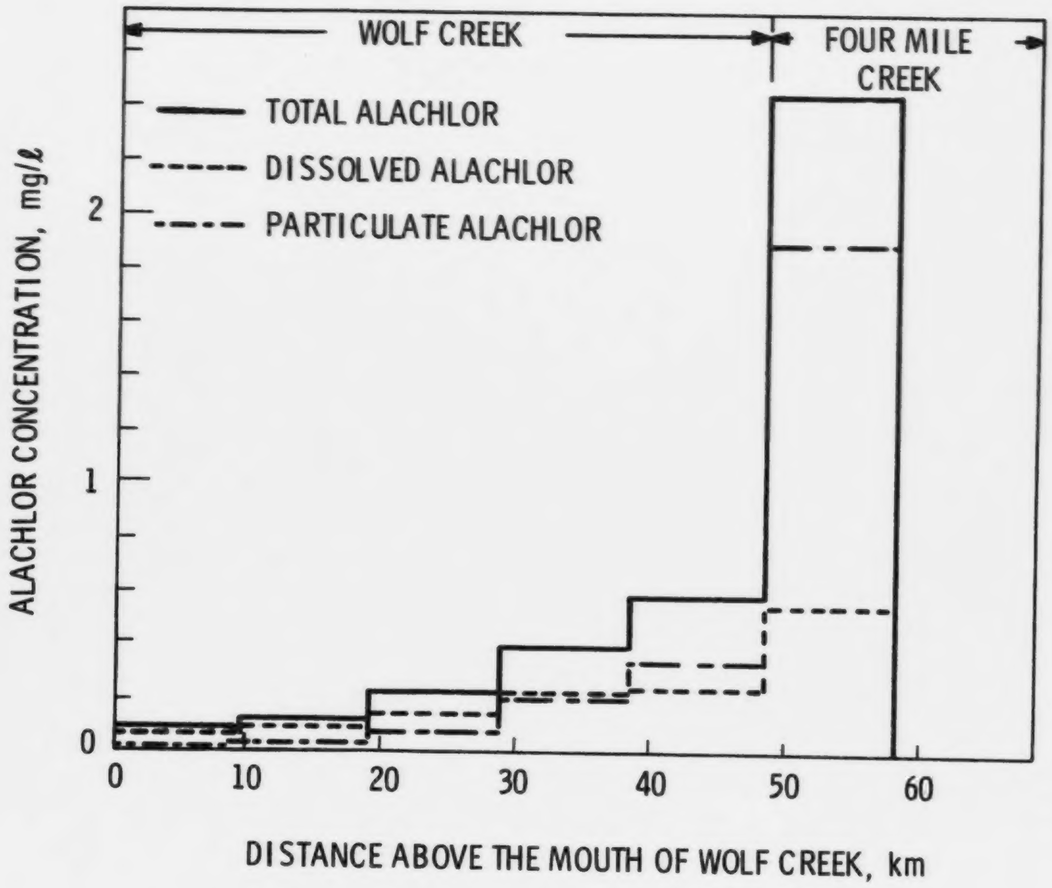


Figure 46. Longitudinal distributions of simulated dissolved, particulate and total alachlor at 6 a.m., June 4, 1973.

indicate a small number of sharp peaks of water discharge, sediment concentration, and concentrations of particulate, dissolved and total alachlor occurred during the three-year period. Comparison of Figures 38, 39 and 40 reveals that most of alachlor transported during May 1972 and May 1973 was in a dissolved form.

There simulation results revealed that high pesticide concentrations in the streams do not directly correlate with peak runoff or soil erosion events, but rather with the time between pesticide application and the first storm event after the application. In other words, pesticide concentrations in the stream have strong seasonal patterns (high peaks in May and June) corresponding to pesticide applications that were closely followed by precipitation causing runoff and soil erosion.

The results imply that the amount of pesticide being transport is controlled by the supply of pesticide on the land surface. Since alachlor degrades very rapidly after application to farm land, significant improvements in water quality can be obtained through the control and curtailment of both runoff and erosion shortly after pesticide application.

As shown in Figure 40, the highest predicted alachlor concentration during the three-year period occurred around the end of May to early June 1973. Detailed simulated flow rate, sediment concentration and concentrations of particulate, dissolved and total alachlor during this period are shown in Figures 41, 42, 43 and 44. As indicated by Figure 44, on June 5, 1973, when the maximum alachlor concentration occurred, sediment carries up to approximately 35% of the total alachlor being transported, while 65% was in a dissolved form, according to the model prediction.

Simulated longitudinal distributions of sediment concentration and concentrations of dissolved, particulate and total alachlor occurring on June 4, 1973, are presented in Figures 45 and 46, respectively.

Instream modeling demonstrates some important effects of sediment transport on pesticide migration:

1. Through adsorption of dissolved pesticides by sediment, immediate biological availability of the pesticide may be reduced.

2. Through deposition of contaminated sediment, pesticide concentrations in a water column will be reduced.

3. However, the contaminated bed sediment then becomes a long-term source of pollution through resuspension and desorption.

The effect of adsorption as described above is demonstrated in Figures 44 and 46. When the maximum alachlor concentration occurred near the mouth of Wolf Creek on June 5, 1973, approximately 35% of the total alachlor was being carried by sediment, while 65% was in a dissolved form that is generally subject to more immediate uptake by aquatic biota (Figure 44). Near the Four Mile Creek Mouth, dissolved and particulate alachlor consisted of 22% and 78% of the total, respectively. Since most of alachlor at the stream edge was in a dissolved form, sediment uptake in the receiving water reduced the dissolved pesticide amount by 78% (Figure 46).

The effect of contaminated sediment deposition is clearly seen in the variation of longitudinal alachlor concentrations in Wolf Creek (Figure 46). The percentage of particulate alachlor to total alachlor steadily decreased from 59% to 8% with the downstream distance in Wolf Creek. The reduction of particulate concentration with the downstream distance was due to the deposition of contaminated sediment before it reached the mouth of Wolf Creek. Another possible cause of particulate contaminant reduction is the dilution of pesticide by clean Wolf Creek water inducing desorption of pesticide from sediment to water. Reduction of total alachlor concentration with distance reflects the particulate alachlor trend.

The effect of sediment migration on contaminant distribution is demonstrated in Figure 47, showing longitudinal particulate alachlor distributions associated with the three sediment-size fractions and their weighted average in the top bed layer after the 3-year simulation. Since it was assumed that initially there was no alachlor in the stream bed, the accumulation of alachlor in the bed must have occurred during the 3-year period through deposition and resuspension of contaminated sediment and direct adsorption and desorption with overlying water. Consequently, even if the use of alachlor is terminated, already contaminated bed sediment will continue to introduce alachlor back to the water column.

Although predicted concentrations of sediment and pesticide obtained by SERATRA seem reasonable, no detailed examination of these results was not possible due to no measured data available.

The dissolved pesticide distribution near the mouth of Wolf Creek River Kilometer 5 shown in Figure 39 was then statistically analyzed by FRANCO for the pesticide risk assessment.

STATISTICAL ANALYSIS AND RISK ASSESSMENT

Case Study of Alachlor

Alachlor was assessed for its known lethal and sublethal effects to fish. The following toxicity information was obtained for Lasso® MCB/C-9, Lasso® E.C., and for alachlor (100% active ingredient). Lasso®(MCB/C-9) was used for the risk assessment process. The Lasso® E.C. formulation was included to help formulate information on channel catfish. The increased toxicity of Lasso® over alachlor demonstrates the probable effects of surfactant synergism.

With the exception of fathead minnow data which are from flow-through measured experimentation, the results below are from static bioassays of nominal (calculated) concentrations. Optional standardization to flow-through, measured concentration for LC50 values is shown below:

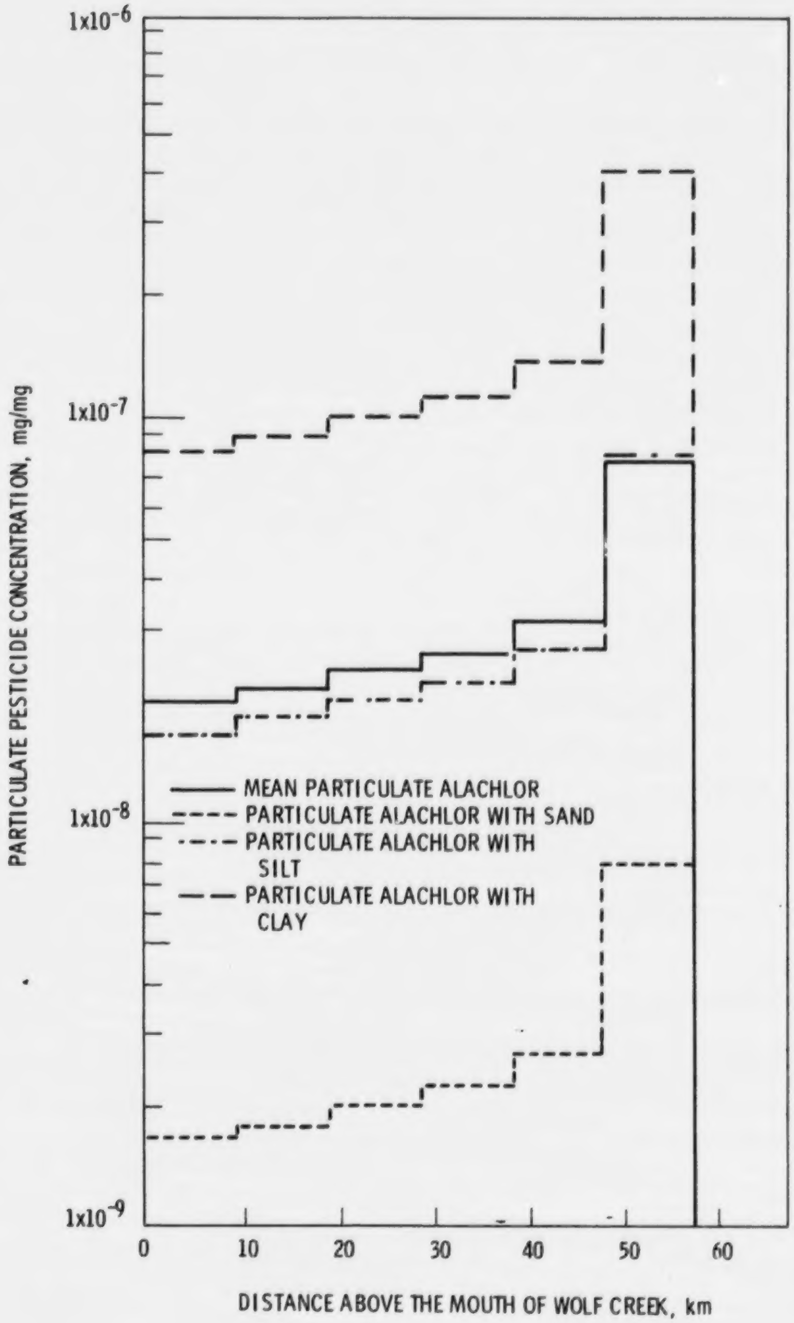


Figure 47. Variations of simulated particulate alachlor in the top bed layer accumulated during the three-year simulation period.

Static value x 0.71 approximates flow through concentration
Nominal value x 0.77 approximates measured concentration
Bluegill 96-hr LC50: 6.2 x 0.71 (static) x 0.77 (nominal) = 3.39
Rainbow 96-hr LC50: 3.7 x 0.71 (static) x 0.77 (nominal) = 2.02

Thus, the acute numbers standardize to roughly half their original concentration values. For lack of direct evidence indicating that these specific values are more correct than the original concentration levels, the original set was employed to continue the risk assessment. However, values obtained by standardization may more closely approximate actual toxic concentration. This emphasizes the necessity of accurate testing techniques and recommends the use of flow-through bioassays of measured concentration for best results.

	LC50 in mg/l			
	24-hr	48-hr	96-hr	Source
Lasso® (MCB/C-9)				
bluegill	16	10	6.2	Monsanto Agricultural Product Co.
rainbow	9.6	7.8	3.7	Monsanto Agricultural Product Co.
Lasso® E.C.				
channel catfish			6.5	Monsanto Agricultural Product Co.
bluegill			13.4	Weed Science Society of America 1979
rainbow			2.3	Weed Science Society of America 1979
Alachlor				
bluegill	13	6.4	2.8	Monsanto Agricultural Product Co.
rainbow	9.2	3.5	1.8	Monsanto Agricultural Product Co.
fathead minnow	8.7	5.8	4.4	(192-hr LC50-2.5) Call et al. 1979

The objective is to evaluate Lasso's® (MCB/C-9) toxicity for bluegill, rainbow, and channel catfish. Sufficient information is provided for only the first two species, so results from Lasso® E.C. and alachlor were used to derive a 96-hr LC50 value for catfish. One would expect the ratios of (MCB/C-9) to Lasso® E.C. data to be similar for rainbow and bluegill. This ratio could then be used to define a value for catfish. Actually, however, there is a large difference in these ratios, possibly due to the different effects of the emulsion formation on the two fish species.

$$\text{Bluegill } \frac{6.2}{13.4} = 0.46 \qquad \text{Rainbow } \frac{3.7}{2.3} = 1.61$$

Use was made of both ratios to calculate a range which may include the true value for catfish.

Catfish 6.5 x 0.46 = 3.0 and 6.5 x 1.61 = 10.5

Assuming the 96-hr LC50 lies between 3.0 and 10.5 mg/l, a geometric mean, based on this range, for convenient handling is calculated as:

Catfish 96-hr LC50: $\sqrt{3.0 \times 10.5 = 5.6}$

The next step is the calculation of 24- and 48-hr LC50 values for catfish to Lasso® (MCB/C-9). As catfish are not closely related to bluegill or rainbow, the slopes from 24-, 48-, and 96-hr LC50 data of bluegill and rainbow were used to derive concentration ranges for catfish.

Slopes

Bluegill	Rainbow
$\frac{6.2 - 16 \text{ mg/l}}{96 - 24 \text{ hr}} = -0.136$	$\frac{3.7 - 9.6}{96 - 24} = -0.082$
$\frac{6.2 - 10}{96 - 48} = -0.079$	$\frac{3.7 - 7.8}{96 - 48} = -0.085$

The ranges generated will be used to approximate the 24 and 48-hr LC50 values for catfish.

96-hr LC50 = 5.6 mg/l

$$\frac{3.0 - X}{96 - 24} = -0.082 \text{ to } -0.136 \qquad \frac{10.5 - X}{96 - 24} = -0.082 \text{ to } -0.136$$

Solving the above equations for X yields

24-hr LC50 = 8.9 to 12.8 mg/l
24-hr LC50 = 16.4 to 20.3 mg/l

Combining these values leads

24-hr LC50 range = 8.9 to 20 mg/l

$$\frac{3.0 - X}{96 - 48} = -0.079 \text{ to } -0.085 \qquad \frac{10.5 - X}{96 - 48} = 0.079 \text{ to } 0.085$$

Solving the above equations for X yields

48-hr LC50 = 6.8 to 7.1 mg/l
48-hr LC50 = 14.3 to 14.6 mg/l

Combining these results leads

48-hr LC50 range = 6.8 to 14.6 mg/l

The geometric mean converts these ranges to points.

24-hr LC50: $\sqrt{8.9 \times 20.3} = 13.4$ mg/l

48-hr LC50: $\sqrt{6.8 \times 14.6} = 10.0$ mg/l

Standardization factors based on the 96-hr LC50 geometric mean of 5.6 mg/l would give these results. Slopes associated with these values are dissimilar to those experimentally derived for bluegill and rainbow.

5.6 x 1.52 = 24-hr LC50 of 8.5

5.6 x 1.23 = 48-hr LC50 of 6.9

The acute data considered most appropriate from the steps above are included here in mg/l. The symbol (^) above a number differentiates it as an estimated (nonexperimental) value.

	24-hr LC50	48-hr LC50	96-hr LC50
Lasso (MCB/C9)			
bluegill	16	10	6.2
rainbow	9.6	7.8	3.7
catfish	$\widehat{13.4}$	$\widehat{10.0}$	$\widehat{5.6}$

No chronic toxicity values were currently available for Lasso® (MCB/C-9). However, recent results of fathead exposure to alachlor show the no-effect level between 0.52 and 1.0 mg/l (Call et al. 1979). Its application factor range is 0.12 to 0.23. Assuming the application factor for Lasso® (MCB/C-9) is the same as for alachlor, the MATC factors can be calculated for the other fish species.

	96-hr LC50		MATC Range
bluegill	6.2	x 0.12 to 0.23 =	0.74 to 1.43
rainbow	3.7	x 0.12 to 0.12 =	0.74 to 0.85
catfish	5.6	x 0.12 to 0.23 =	0.67 to 1.29

Had an experimental MATC value for alachlor been unavailable, selection of an arbitrary no-effect level would have been necessary. This procedure is also given, and comparisons between the results of both methods can be examined. Since Lasso® is not known to be either persistent or cumulative in its effects under normal conditions, the selected arbitrary application factors are 0.05 for a 24-hour average and 0.1 for a temporary level. Use of the 24-hour average should give a conservative estimate of the MATC value:

96 hr-LC50 x AF = MATC
bluegill 6.2 x 0.05 = 0.31
rainbow 3.7 x 0.05 = 0.19
catfish 5.6 x 0.05 = 0.28

In this case the arbitrary MATC values produce a lower, more conservative measurement of the no-effect level.

The rainbow trout species (Salmo gairdneri) was chosen for the methodology illustration with the following curves using LC50 data and the MATC value.

1. The SERATRA cutoff.

2. The MATC line (see Figure 48).

3. The LC50-MATC curve (see Figure 49).

The six pairs of points used for each curve are listed below. Concentrations are given as kg/m^3 (= 1000 ppm). While six points were used to define such curves, some could have been defined with fewer points.

1. Curve 1 uses the concentration of 1.0×10^{-9} at each of the time steps which include 0.5, 24, 48, 96, 168, and 336 hours.

2. Curve 2 uses the concentration of 1.9×10^{-4} at each time step including 0.5, 24, 48, 96, 168, and 336 hours.

3. Curve 3 uses the following (duration, concentration) pairs: (0.5, 0.0096), (24, 0.0096), (48, 0.0078), (96, 0.0037), (96, 0.00019), (336, 0.00019).

The mouth of Wolf Creek has been used for modeling the concentration-duration aspects of the FRANCO code.

The Exceedance Summary for alachlor includes several parameters for each curve. In this case the summary shows that the duration-concentration levels of alachlor were insufficient to register as an event. No duration exceeded even the MATC function, and therefore, global exceedance is 0%. Investigation of the data generated under each category confirms that the minimum given value for alachlor, its estimated MATC concentration of 1.9×10^{-4} kg/m^3 (or 0.19 ppm), is not exceeded at any time (see Figure 39).

Thus, it is concluded that dissolved concentrations of alachlor near the mouth of Wolf Creek is less than the MATC for the three years modeled and should present no direct threat of toxicity to the rainbow trout or other species with a MATC greater than 0.19 ppm, assuming no unusual circumstances increasing the effective concentration or effective toxic level.

Case Study of Toxaphene

Alachlor was chosen in the modeling study because of its available field data. The computer evaluation demonstrated that alachlor should not have caused damage to rainbow trout. To more clearly illustrate possible applications of the model, toxaphene was chosen as a second pesticide for the risk assessment.

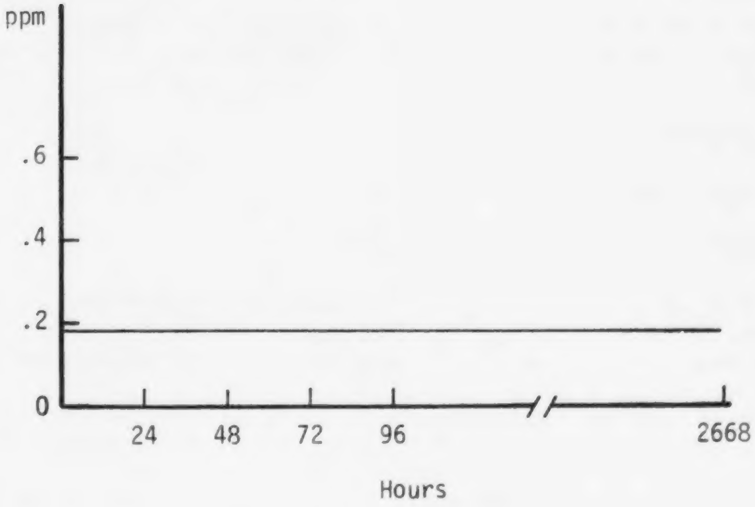


Figure 48. MATC line for alachlor.

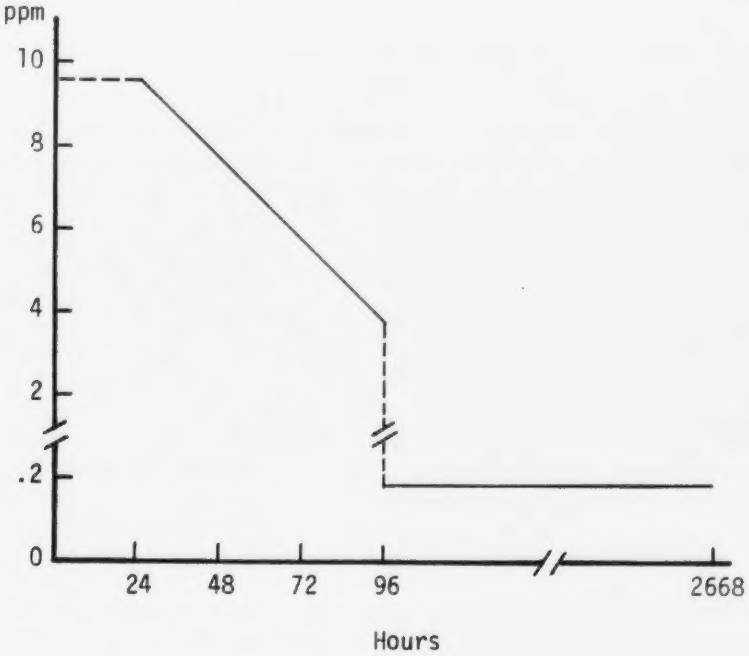


Figure 49. LC50 - MATC curve for Lasso®.

Toxaphene, a chlorinated hydrocarbon, is very persistent in soil and water and may be bioconcentrated to a high degree. Its addition to lakes has been shown to cause toxicity for ten years. Its persistence in soils has been cited as 4 to 16 years. Its solubility of 1.5 ppm and its estimated Kd value of 5×10^4 differ considerably from those of alachlor. One would expect toxaphene to be strongly sorbed to the sediments, raising interest in modeling toxaphene in sediments as well as the dissolved state.

The risk assessment procedure for toxaphene is based on the same stream concentrations as generated for alachlor. This is done only as an example and is not meant to imply actual concentration levels for toxaphene. The physical and chemical properties of toxaphene are considerably different from alachlor.

Toxicity data used here are from pages B-27 and B-28 in the Appendix B. The following species have been selected to illustrate the assessment procedure for toxaphene. Again, the values are expressed as mg/l.

Without knowledge of the technique of each bioassay, one cannot make a logical decision on the necessity for standardization of the values. For the sake of this example, it was assumed that the following numbers represent actual toxicity values.

	24-hr LC50	48-hr LC50	96-hr LC50
Coho Salmon	0.0130	0.0105	0.0094
Chinook Salmon	0.0079	0.0033	0.0025
Rainbow Trout	0.0115	0.0084	0.0084
Brown Trout			0.003
Carp			0.004
Fathead Minnow			0.014
Channel Catfish			0.013
Guppy			0.020
Bluegill Sunfish			0.0035
Largemouth Bass			0.002

The minimum three data points are available in Appendix B for only three species. The rest must be derived from these or from toxicity data for related pesticides.

The brown trout is related by genus to the rainbow trout so the slope of the 24-96 and 48-96 hour segments from the rainbow were used to estimate the 24- and 48-hr LC50 values for the brown trout.

$$\text{rainbow } \frac{0.0084 - 0.0115}{96 - 24} = -4.3 \times 10^{-5}$$

$$\frac{0.0084 - 0.0084}{96 - 48} = 0$$

brown $$\frac{0.003 - X}{96 - 24} = -4.3 \times 10^{-5}$$

24-hr LC50 = 0.0061 mg/l

$$\frac{0.003 - X}{96 - 48} = 0$$

48-hr LC50 = 0.003 mg/l

None of the other species other than the salmon are related to the trout except by class, so other steps are used to estimate the 24- and 48-hr LC50 values where they are missing.

The use of the geometric mean of the slopes will be demonstrated to approximate the unknowns. There is no way of knowing whether values calculated in this manner fall within the range provided by the other slopes. However, the chances are improved with a larger number of experimental values already established for each time interval. The use of estimated values from previous steps introduces more probability for error and should be avoided. In this example, the experimental values obtained for coho, chinook, and rainbow are used.

	24 - 96-hr Slope	48 - 96-hr Slope
coho salmon	-5.0×10^{-5}	-2.3×10^{-5}
chinook salmon	-7.5×10^{-5}	-1.7×10^{-5}
rainbow trout	-4.3×10^{-5}	0
Range	-7.5×10^{-5}	-2.3×10^{-5}
	to -4.3×10^{-5}	to 0.0
Geometric mean	-5.44×10^{-5}	-1.58×10^{-5}
		(as $\sqrt[3]{-2.3 \times 1.7 \times 10^{-10}}$)

Applying these values to the fish with incomplete data sets results in the following ranges and geometric means:

Example:

carp $$\frac{0.004 - X}{96 - 24} = -7.5 \times 10^{-5} \text{ to } -4.3 \times 10^{-5}$$

	Range	Geometric Mean
24-hr LC50 =	0.0071 to 0.0094	0.0079

Estimated Geometric Means as mg/l:

	24-hr LC50	48-hr LC50	96-hr LC50
carp	0.008	0.005	0.004
fathead minnow	0.018	0.015	0.014
channel catfish	0.017	0.014	0.013
guppy	0.024	0.021	0.020
bluegill sunfish	0.0077	0.0040	0.0035
largemouth bass	0.006	0.002	0.002

The values above can be contrasted with those calculated using 24, 48, and 96-hr standardization factors:

96-hr LC50 x 1.52 = 24-hr LC50

96-hr LC50 x 1.23 = 48-hr LC50

	24-hr LC50	48-hr LC50	96-hr LC50
carp	0.006	0.005	0.004
fathead minnow	0.021	0.017	0.014
channel catfish	0.020	0.016	0.013
guppy	0.030	0.025	0.020
bluegill sunfish	0.0053	0.0043	0.0035
largemouth bass	0.003	0.0025	0.002

In this case the two methods produced similar results. Because there are some experimental data sets from which slopes can be derived, the estimated geometric mean values were used as the most likely to represent the actual values. This yields the following toxaphene acute toxicity data as mg/l for use with the probability model:

	24-hr LC50	48-hr LC50	96-hr LC50
coho salmon	0.0130	0.0105	0.0094
chinook salmon	0.0079	0.0033	0.0025
rainbow trout	0.0115	0.0084	0.0084
brown trout	$0.\hat{0}06$	$0.\hat{0}03$	0.003
carp	$0.\hat{0}08$	$0.\hat{0}05$	0.004
fathead minnow	$0.\hat{0}18$	$0.\hat{0}15$	0.014
channel catfish	$0.\hat{0}17$	$0.\hat{0}14$	0.013
guppy	$0.\hat{0}24$	$0.\hat{0}21$	0.020
bluegill sunfish	$0.\hat{0}077$	$0.\hat{0}040$	0.0035
largemouth bass	$0.\hat{0}06$	$0.\hat{0}02$	0.002

The symbol (^) indicates estimated values.

Chronic toxicity values for toxaphene stated as MATC ranges have been located for the fathead minnow and channel catfish.

fathead minnow $0.000025 < \text{MATC} < 0.000054$
channel catfish $0.000049 < \text{MATC} < 0.000072$

Application factor ranges are calculated below from MATC and 96-hr LC50 data.

MATC range/96-hr LC50 = AF range
fathead minnow 0.000025 to $0.000054/0.014 = \text{AF}$
$\text{AF} = 0.0018 - 0.0038$
channel catfish 0.000049 to $0.000072/0.013 = \text{AF}$
$\text{AF} = 0.0038 - 0.0055$

Carp and fathead minnows are related at the family level so the application factor derived for the fathead minnow will be applied to the 96-hour LC50 point for carp.

0.004×0.0018 to $0.0038 = \text{MATC}$
$0.0000072 < \text{MATC} < 0.0000152$

For the unrelated species the high and low values from fathead minnow and channel catfish can be used to set a range. The geometric mean can be used to convert the ranges to points.

AF range = 0.0018 - 0.0055

Toxaphene is known to be very persistent and would require the use of the more conservative arbitrary application factor of 0.01 for a 24 hour average if no experimental data were available.

Geometric means, as well as MATC experimental and derived ranges, have been included in this list of chronic toxaphene toxicity as mg/l.

	< MATC Range <		Geometric Mean
coho salmon	1.7×10^{-5}	5.2×10^{-5}	3.0×10^{-5}
chinook salmon	0.45×10^{-5}	1.4×10^{-5}	0.79×10^{-5}
rainbow trout	1.5×10^{-5}	4.6×10^{-5}	2.6×10^{-5}
brown trout	0.54×10^{-5}	1.7×10^{-5}	0.96×10^{-5}
carp	0.72×10^{-5}	1.5×10^{-5}	1.3×10^{-5}
fathead minnow	2.5×10^{-5}	5.4×10^{-5}	3.7×10^{-5}
channel catfish	4.9×10^{-5}	7.2×10^{-5}	5.9×10^{-5}
guppy	3.6×10^{-5}	11.1×10^{-5}	6.3×10^{-5}
bluegill	6.3×10^{-5}	1.9×10^{-5}	3.5×10^{-5}
largemouth bass	3.6×10^{-5}	1.1×10^{-5}	2.0×10^{-5}

Lethal and sublethal data was used to assess environmental damage to rainbow trout (Salmo gairdneri) from toxaphene exposure. Because of toxaphene's extreme toxicity to fish, seven curves were chosen, in addition to the SERATRA cutoff, to demonstrate the kind of additional information which can be gained. All are illustrated in Figures 50 through 57.

1. Curve A is the SERATRA cutoff value.
2. Curve B is the MATC for rainbow trout.
3. Curve C is the least conservative lethality curve.
4. Curve D is the most conservative curve designated as LC50-MATC.
5. Curve E is intermediate between curves C and D.
6. Curve F considered the results of the LC50-MATC line segments after 24 hours.
7. Curve G generates results exceeding the LC50-MATC lines beginning at 48 hours.
8. Curve H describes exceedance of the MATC starting at 96 hours.

The six pairs of points used for each curve are listed with duration in hours and concentrations as Kg/m^3.

1. Curve A uses the concentration of 1.0×10^{-9} Kg/m^3 at each of the following durations: 0.5, 24, 48, 96, 168, and 336 hours.
2. Curve B uses the most conservative MATC endpoint for rainbow trout of 1.5×10^{-8} Kg/m^3 . Time durations are again 0.5, 24, 48, 96, 168, and 336 hours.
3. Curve C includes the following sets of points: $(24, 1.15 \times 10^{-4})$, $(24, 1.15 \times 10^{-5})$, $(48, 8.4 \times 10^{-6})$, $(96, 8.4 \times 10^{-6})$, $(168, 8.4 \times 10^{-6})$, and $(336, 8.4 \times 10^{-6})$.
4. Curve D is described by the following points: $(0.5, 1.15 \times 10^{-5})$, $(24, 1.15 \times 10^{-5})$, $(48, 8.4 \times 10^{-6})$, $(96, 8.4 \times 10^{-6})$, $(96, 1.5 \times 10^{-8})$, and $(336, 1.5 \times 10^{-8})$.
5. Curve E has points at $(0.5, 1.15 \times 10^{-5})$, $(24, 1.15 \times 10^{-5})$, $(48, 8.4 \times 10^{-6})$, $(96, 8.4 \times 10^{-6})$, $(168, 8.4 \times 10^{-6})$, and $(336, 8.4 \times 10^{-6})$.
6. Curve F includes the following points: $(24, 1.15 \times 10^{-4})$, $(24, 1.15 \times 10^{-5})$, $(48, 8.4 \times 10^{-6})$, $(96, 8.4 \times 10^{-6})$ $(96, 1.15 \times 10^{-8})$, and $(336, 1.5 \times 10^{-8})$.

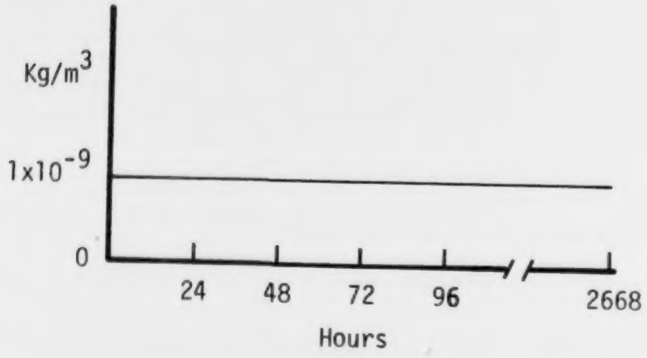


Figure 50. Curve A - SERATRA Cutoff value.

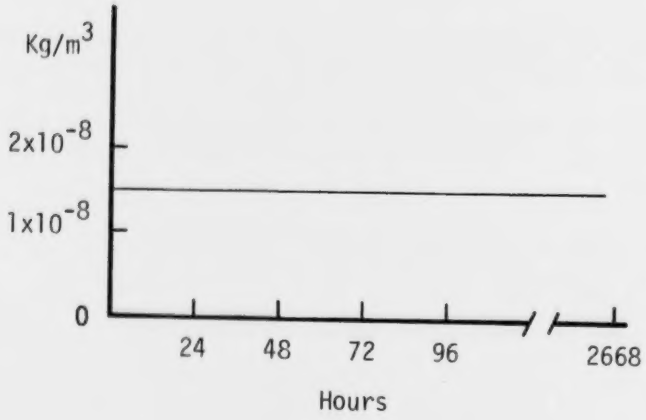


Figure 51. Curve B - MATC line.

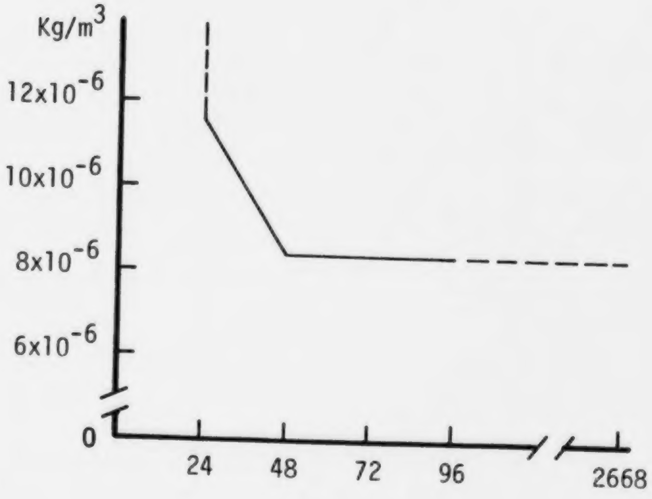


Figure 52. Curve C - Lethality curve least likely to indiciate mortality.

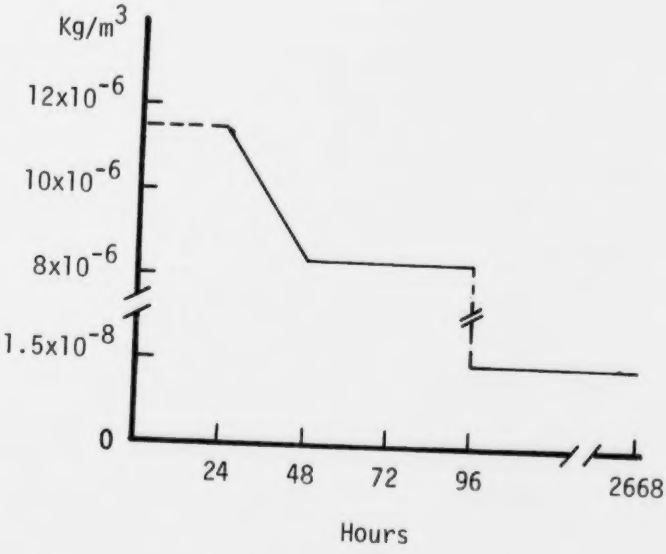


Figure 53. Curve D - LC50 - MATC conservative curve.

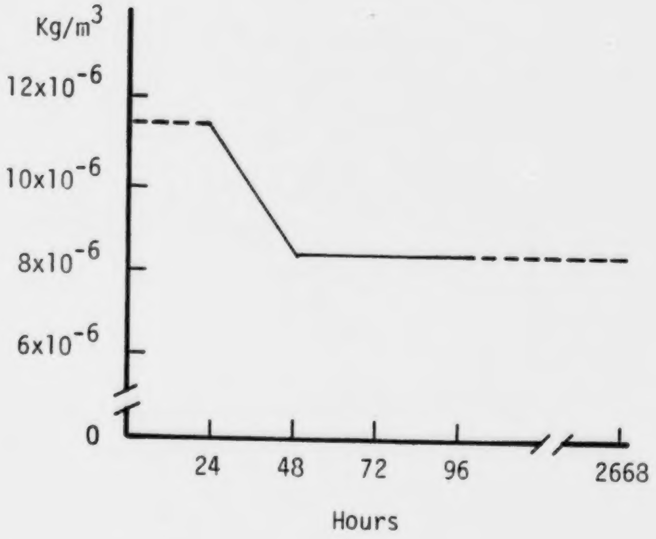


Figure 54. Curve E - LC50 - alternative curve.

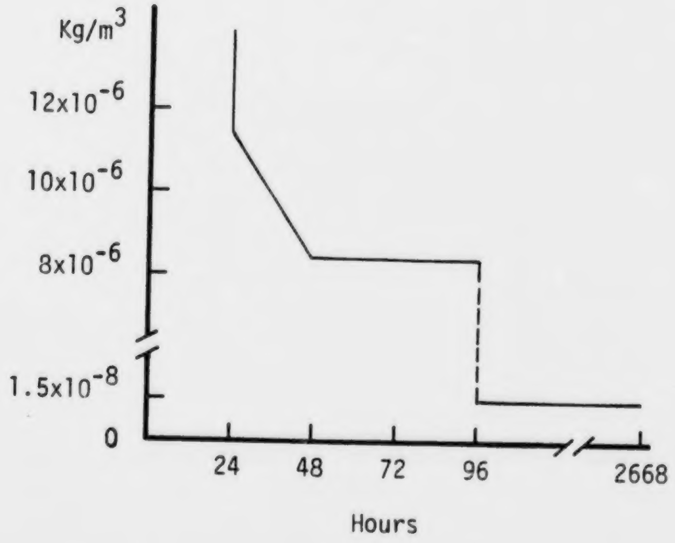


Figure 55. Curve F - LC50 - MATC curve for durations exceeding 24 hours.

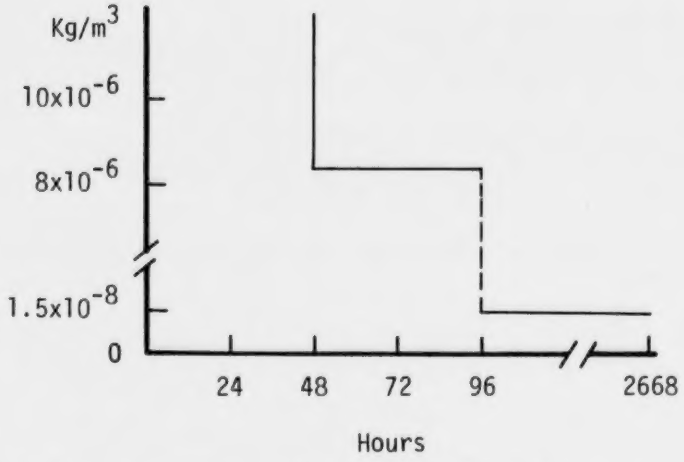


Figure 56. Curve G - LC50 - MATC curve for durations exceeding 48 hours.

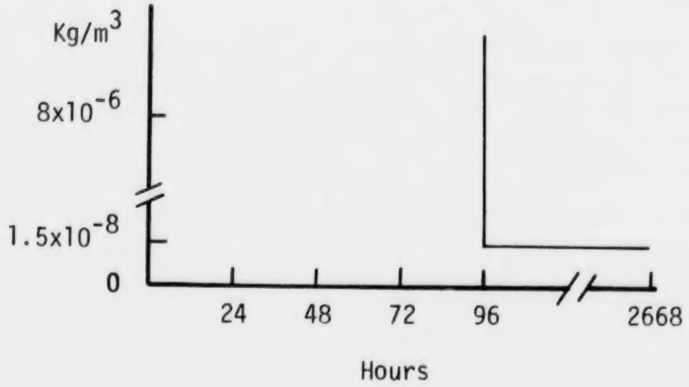


Figure 57. Curve H - MATC exceedance for durations greater than 96 hours.

7. Curve G has the following points: $(48, 1.15 \times 10^{-4})$, $(48, 1.15 \times 10^{-5})$, $(48, 8.4 \times 10^{-6})$, $(96, 8.4 \times 10^{-6})$, $(96, 1.5 \times 10^{-8})$, and $(336, 1.5 \times 10^{-8})$.

8. Curve H is described by the following points: $(96, 1.15 \times 10^{-4})$, $(96, 1.5 \times 10^{-5})$, $(96, 8.4 \times 10^{-6})$, $(96, 1.5 \times 10^{-8})$, and $(336, 1.5 \times 10^{-8})$.

The exceedance summary inumerates the following curve results for the mouth of Wolf Creek.

Curve	Events	Total Duration	Global Exceedance
A	9	4160 hr	16.23%
B	12	3828	14.93
C	2	314	1.23
D	6	3461.5	13.50
E	2	314	1.23
F	6	3461.5	13.50
G	6	3461.5	13.50
H	6	3461.5	13.50

1. Curve A - 16.2% of total time divided into nine events exceeded the SERATRA cutoff value.

2. Curve B - Twelve events, comprising 14.9% of the modeling time, exceeded the MATC designated line of 1.5×10^{-5} ppm. Had the high MATC endpoint of 4.6×10^{-5} ppm or the geometric mean value of 2.6×10^{-5} been selected to represent the MATC, the global exceedance value would have been reduced to 14.0% and 14.5%, respectively.

   Of the twelve events, six lasted for more than 96 hours and accounted for 90.4% of the time exceeding the MATC. The longest event of 1257.5 hours began at time-step 16496 and lasted through time-step 19011. Clearly, 1257.5 hours at concentrations above the MATC suggests concern for sublethal effects. Damage may largely depend on life stages present during such long-term events.

3. Curve C - The lethal curve based on known LC50 values was exceeded in two events lasting a total of 314 hours, which was 1.2% of the total modeling time. A breakdown of the event durations shows 196.5 hours for the first event and 117.5 hours for the second. The assumption of no lethality prior to D suggests that, in spite of values exceeding C_1 at D_1, no median fish kill occurs.

4. Curve D - The MATC incorporated with the LC50 curve is represented by six events lasting 3461.5 total hours for a global exceedance of 13.5%. Those events, represented by curve B (lasting more than 96 hours) and by curve C, are included in this percentage.

5. Curve E - This curve is equivalent to curve C in this example. This may seem surprising since two events had concentrations greater than 1.5×10^{-5}. However, these concentrations lasted for 96 and 168 hours, which is long enough to be counted in curve C. The assumption that $C_o = C_1$ indicates that most rainbow trout would not survive the first 24 hours of exposure at concentration levels greater than C_1. Had concentrations greater than 1.15×10^{-5} been evident for durations less than 24 hours, the global exceedance for curve E would be greater than curve C by the area represented by $C > C_1$ and $D > D_1$.

6. Curve F - Results of curve F are identical to curve D because concentrations greater than C_1 at durations less than D_1 exceed the 24 hour minimum function time.

7. Curve G - This curve again shows the same results as curve D. Both events exceeding curve G are also exceeded by curves D and F.

8. Curve H - Once more, the function represented by $C \geq 1.5 \times 10^{-5}$ ppm at $D \geq 94$ hours is exceeded six times for a total of 13.5%. Had any of the six events noted in curves F or G above lasted for less than 96 hours, the exceedance of curve H would be reduced proportionally.

A summary of the curves is shown in Figure 58. Concentrations are within safe limits 85.1% of the total modeling time. Concentration-duration values fell within the potential lethal/sublethal (<LC50) zone 13.7% of the time. Lethality as measured by the LC50 curve was exceeded 1.2% of the total modeling time.

If this toxaphene example were a real case, the summary should be used as a tool in the assessment of potential effects. Actual interpretations must consider all other pertinent factors concerning the situation in conjunction with the concentration summary.

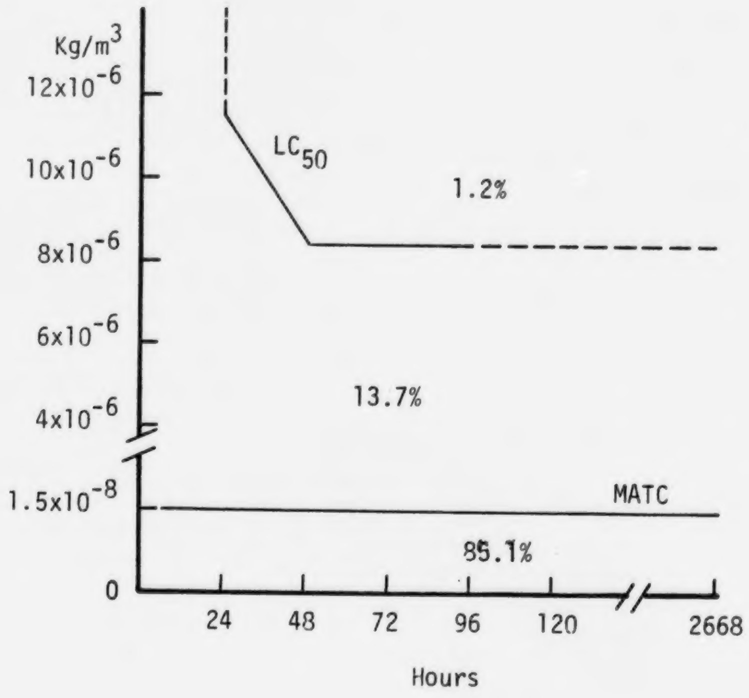


Figure 58. Summary of toxaphene curves.

SECTION 6

EVALUATION OF THE CMRA METHODOLOGY

The CMRA Methodology was developed and was applied to the Four Mile and Wolf Creek area in Iowa to examine the applicability and limitation of this methodology. The methodology is general enough to evaluate the migration and risk assessment as applied to a wide range of pesticides, agricultural lands, receiving streams and aquatic biota. For example, this methodology could be used to select optimum pesticide application practices including timing and doses.

The application of the methodology to to Four Mile and Wolf Creeks revealed that in general, the CMRA Methodology is capable of simulating migration and fate of a pesticide and its associated risk to aquatic biota. However, accuracy of predicted results depends largely on the availability of data. The application exercise also revealed that it requires a rather extensive effort to evaluate pesticide movements and its risks. Furthermore, due to a general lack of data, calibration and verification of the models, especially portions concerning pesticide transport, adsorption/desorption, and degradation were not fully performed and that further testing of the methodology is required. Also a FRANCO output of probability of acute and chronic damages to aquatic biota must be supplemented by other pertinent information on pesticide characteristics, environmental stress, life stages of biota, etc., to obtain more comprehensive risk assessment. Applicability and limitations of each of the four components of the CMRA Methodology are discussed below.

OVERLAND PESTICIDE MODELING

The ARM model was specifically developed as a tool to evaluate the quantity and water quality of runoff coming from agricultural areas, as well as the impacts of alternative management practices. The model's capability to continuously simulate nonpoint source pollution processes makes it useful for evaluating both short- and long-term migration of pesticides overland. The application of ARM is limited primarily by the availability of data for model calibration and by the size of an area which can be accurately modeled in a single simulation. Given the state-of-the-art of modeling nonpoint source pollution from agriculture, ARM is the most appropriate pesticide loading technique for this methodology.

INSTREAM PESTICIDE MODELING

The unsteady, two-dimensional model, SERATRA, which is used for the instream pesticide modeling, includes all important mechanisms of both dissolved and particulate pesticide transport phenomena, such as convection and dispersion of pesticides, interaction of pesticides with sediment (adsorption and desorption of pesticides with sediment, and transport, deposition and resuspension of particulate pesticides associated with sediment), and chemical (oxidation, hydrolysis, and photolyses) and biological degradation of pesticides and volatilization. Since SERATRA is one of the few tested models capable of simulating both dissolved and particulate contaminants with sediment-contaminant interactions, it is well suited to this methodology. SERATRA is applicable to the nontidal rivers and narrow lakes where vertical and longitudinal distributions are of interest, but is not suitable to estuaries and coastal areas where lateral and longitudinal distribution may be of concern. Another important aspect of this portion of the methodology is that SERATRA provides vertical and longitudinal distributions of dissolved and particulate pesticides, as well as the pesticide accumulation in the stream bed. However, because of the rather limited knowledge of pesticide toxicity, only cross-sectionally averaged dissolved pesticide concentrations are used for the risk assessment. Additional data collection for pesticide toxicity may make it possible to take the full advantage of detailed simulation results of SERATRA in the future. Lack of field data needed for the model calibration is the major difficulty apparent when SERATRA is applied to an actual study area. Another limitation is the limited applicability of EXPLORE-I to very small streams. Furthermore, since SERATRA is a two-dimensional (longitudinal and vertical) model and EXPLORE-I is one-dimensional (possibly used as longitudinal and vertical two-dimensional model), compatibility between SERATRA and EXPLORE-I is less than ideal.

STATISTICAL ANALYSIS AND RISK ASSESSMENT

The risk assessment procedure uses a finite number of parameters to summarize the pesticide concentration within the watershed of interest and to predict the probability of toxic effects to indigenous fish species. Of necessity, the risk assessment procedure must be simplistic compared to the environmental complexities found within the actual system. The acceptance, or at least acknowledgement, of certain assumptions used in this procedure allows for the prediction of environmental hazards to fish based on those assumptions.

Several important limitations exist in the risk assessment portion of the methodology. Some of the major ones are these:

1. Laboratory bioassays are assumed applicable to the prediction of field toxicities.

2. Synergistic effects of pesticides with river water quality parameters are ignored for lack of information.

3. Bioconcentration and biomagnification properties with predator-prey relationships were not assessed.

4. Interpretation of sublethal effects based on exceedance of the MATC may overestimate hazards.

5. Effects of ingesting pesticides from the suspended fraction and from bottom sediments have not been addressed.

6. Avoidance behavior and migration resulting from pesticide concentration in the water needs investigation.

7. Assessment for resistant or susceptible strains requires identification of such properties for modification of risk assessment input data.

The FRANCO program is very flexible in its risk assessment aspects. The output describes pesticide concentration as the number of times a given value (C_i,d_j) is exceeded, the percentage of total time (C_i,d_j) exceeded, and individual and total time durations when the concentration for a particular river segment exceeds (C_i,d_j). It also computes the percentage of total time the designated function has been exceeded. The model has been demonstrated using only the dissolved portion of pesticide. The program is also capable of assessing the pesticide concentration in the suspended particulate and bed sediment fractions.

The CMRA Methodology was used specifically with fish species to graph the LC50 curve and the MATC and measure its exceedance. However, any other measure of effects may be used instead, such as LC10 or LC90 values. Confidence limits are especially good for indicating a probability range of toxicity. The curve may be partitioned into acute and chronic sections or described as short-term and long-term effects with time boundaries indicated by the methodology user to best fit the situation. The selection of input values may be changed in accordance with the needs. However, the user must be cautioned to make appropriate interpretations based on the assumptions used for data input.

In spite of the limitations inherent in FRANCO, there are real benefits associated with the modeling procedure for predicting the extent of environmental hazards. It has defined some of the problems which may be resolved in the future by one of at least three possible methods. Addition of new mathematical relationships may allow for modeling parameters which more closely fit field conditions. Improvement of data collection systems to fit modeling needs may reduce present model uncertainties. The use of more appropriate hazard indicators and resultant interpretations will improve the predictive ability of the modeling system.

MODELING FLEXIBILITY

Although, as discussed above, the CMRA Methodology consists of four components, the models can be used in different combinations depending on the problems. However, the statistical analysis and risk assessment based on FRANCO must be used together. Examples of combined uses are as follows:

1. If the migration and risk assessment of a toxic contaminant are of concern only at a stream edge, FRANCO can be used to summarize ARM results.

2. If a toxic contaminant is directly discharged to a receiving water body, only EXPLORE-I, SERATRA, and FRANCO are required to evaluate transport and risk assessment.

3. If there are continuous measurements of toxic chemical concentrations available and only the risk assessment is needed, FRANCO alone can be used.

4. If the receiving water bodies are estuaries or coastal waters, SERATRA can be replaced by other appropriate sediment-contaminant models such as FLESCOT and FETRA (Onishi and Wise 1978).

SECTION 7

SIMPLIFIED STATISTICAL METHODOLOGY

Overland and instream pesticide concentrations were statistically examined to study whether pesticide concentration patterns can be expressed by statistical distributions. In this case, gamma, normal and log-normal distributions were selected for testing. This task was conducted to determine if a simpler pesticide assessment methodology which relies only on the statistical nature on precipitation, watershed characteristics, and receiving water body characteristics, could be developed to replace the more detailed computer-model-based CMRA Methodology, as described in Section 4.

The principal steps in the development of any simplified statistical methodology are the statistical summarization of the system input (precipitation), the statistical summarization of the system output (e.g., dissolved, particulate, and total pesticide concentrations) and a simple procedure for predicting the output from the input. The development of these steps begins by first determining the information desired. The stated objective is the frequency of occurrence and duration of given pesticide concentrations. In Subsection 4.2 seven specific summary measures are given to meet this objective. One particular measure, $P_T[C \geq C_i]$, gives the relative frequency of occurrence of simulated concentrations greater than or equal to specified concentration levels. This measure was chosen for the simplified statistical methodology, because it is one of the simplest summaries of a concentration time series.

The FRANCO program summarizes the time series of instream dissolved, particulate and total (sum of dissolved and particulate pesticides) pesticide concentrations. The series is characterized by periods when pesticide concentration is lower than the chosen SERATRA cutoff value, and other periods when runoff events cause the concentration to increase above this value. The cutoff value is selected to represent the point below which the simulated concentration values are due to limitations on the numerical accuracy of the model and the computer. Hence, time periods below this concentration are considered to be zero. As a result the relative frequency of pesticide concentration consists of two parts: A discrete part at the SERATRA cutoff value with an associated frequency that estimates the percent of the time the concentration is considered to be zero and a continuous part that summarizes the relative frequency of concentrations above the cutoff value.

Let C_1 equal zero, C_2 equal the cutoff value and the remaining C_i chosen such that $C_3 < C_4 < . . . < C_m$. Using the notation introduced in

Section 4.2, this choice results in $P_T[C \geq C_1] = 1$ and $P_T[C \geq C_2]$ equal to the relative frequency the simulated concentra- tion was greater than or equal to the cutoff value.

Define

$$G(C) = pF(C) + (1-p)I(C)$$

where $p = P_T[C \geq C_2]$ is the relative frequency of concentrations occurring above the cutoff value, $I(C)$ is a discrete cumulative frequency function with probability one at the cuttoff value, and $F(C)$ is a continuous distribution function.

The investigation of the feasibility of a simplified statistical methodology is based on analyzing the cumulative distribution function F(x) resulting from the dissolved, particulate and total pesticide concentration time series from SERATRA for instream and ARM for stream-edge. The same model can also be applied to the stream discharge and overland runoff. The latter tow can then be compared to an analysis of precipitation data. These analyses form the basis for discussing the feasibility of a simplified statistical methodology. Each of these analyses are individually discussed, followed by a discussion of their interrelationships. The dissolved, particulate and total pesticide concentrations (in kg/m^3) simulated by SERATRA near the mouth of Wolf Creek (River Kilometer 5) is statistically summarized below.

During the three-year period starting June 1971 the dissolved pesticide concentration was greater than the cutoff value of 1.0×10^{-9} for 16.23 percent of the time. Hence p is estimated as 16.23. The continuous part F(C) of the cumulative distribution function G(C) is well represented by the log-normal distribution. A probability plot construction from the cumulative frequency concentration data illustrates this fit in Figure 59. Similar probability plots using the normal and gamma distributions as alternative choices did not result in the expected straight line plot characteristic when the data fits a particular probability distribution. The log-normal probability density function is:

$$f(X) = \frac{1}{X\sigma\sqrt{2\mu}} e^{-\frac{1}{2}(\ln X - \mu)^2/\sigma^2} \qquad X > o.$$

Stated in this form, the parameters μ and σ^2 are estimated by:

$$\hat{\mu} = \frac{\sum_{i=1}^{n} \ln X_i}{n}$$

$$\hat{\sigma}^2 = \frac{\sum_{i=1}^{n} (\ln X_i - \hat{\mu})^2}{n - 1}$$

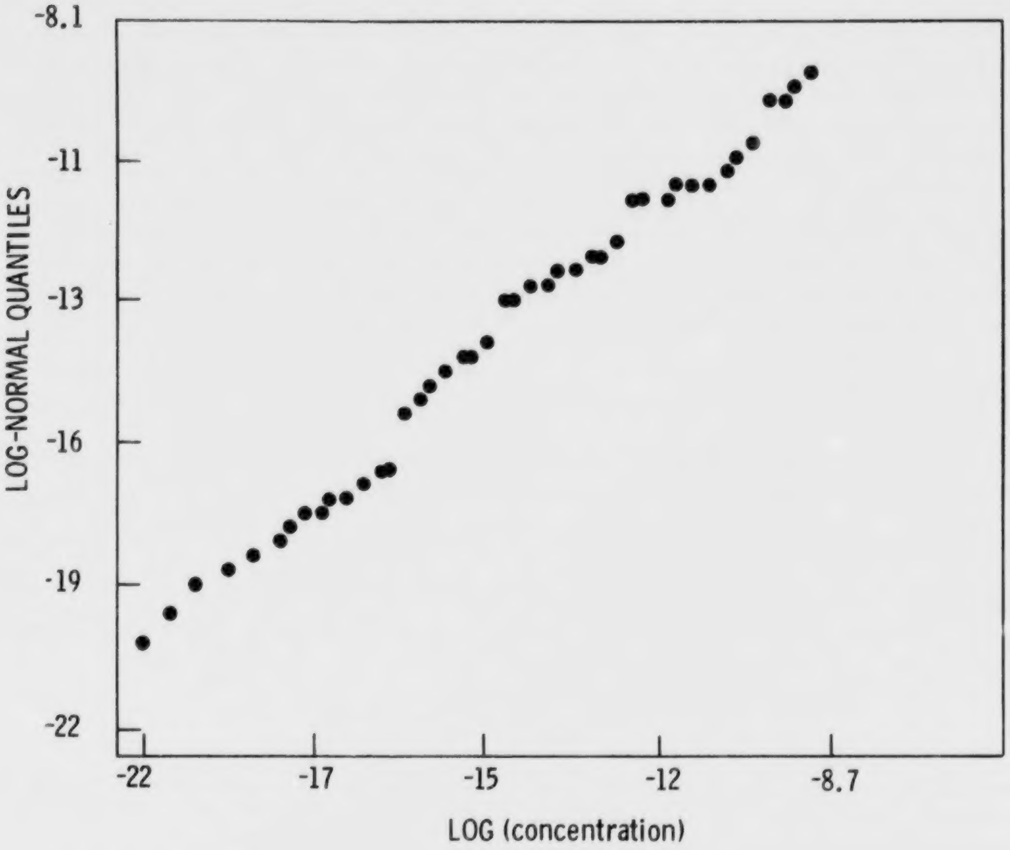


Figure 59. Log-normal probability plot for dissolved pesticide concentration at Wolf Creek River Kilometer 5 (μ = 14.83, σ = 2.26)

where n is the number of concentrations greater than the SERATRA cutoff value and X_i are the simulated dissolved pesticide concentrations for those time steps. In this case the estimates are $\hat{\mu}$ = -14.83 and $\hat{\sigma}$ = 2.26. The mean and variance of the log-normal distribution are:

$$E(X) = e^{\mu + \sigma^2/2}$$

$$Var(X) = E(X)^2 \left[e^{\sigma^2} - 1 \right]$$

Using the estimated values for μ and σ^2, the estimates are $\hat{E(X)}$ = 4.66 x 10^{-6} with a standard deviation of 5.97 x 10^{-5}.

The statistical distribution summary for the dissolved pesticide concentration is completed by the program FRANCO. The distribution parameter estimates are obtained from all concentrations greater than or equal to the SERATRA cutoff value. Because of the number of time steps involved, these estimates are computed by summarizing the data with a flow through technique that does not require all the data to be present at once. In constructing the probability plots ,a modification of the standard procedure, such as described by Hann (1977), was necessary. It was not feasible for all data points to be plotted individually for the probability plot. To overcome this difficulty the data were accumulated as an empirical cumulative distribution function with up to 50 intervals used for the concentration. The probability plot was constructed using those values. The effect on the plot is minimal if these concentration values are appropriately selected to result in approximately an equal number of time steps in each interval. The interpretation of the plot is not affected.

The dissolved pesticide concentration at Wolf Creek River Kilometer 5 is adequately summarized by the mixed distribution:

$$G(C) = 0.1623LN(C;-14.83,2.26) + .8377I(C)$$

where

$$I(C) = \begin{cases} 1 & C \leq 1.0 \times 10^{-9} \\ 0 & C > 1.0 \times 10^{-9} \end{cases}$$

and $LN(C;\mu,\sigma)$ denotes the log-normal distribution with parameters μ and σ. A severe limitation of this summary is the total loss of all information concerning the actual time sequence of the concentrations.

A similar analyses of computed results of SERATRA simulation at Four Mile Creek River Kilometer 5 was completed. A mixed distribution using the log-normal distribution for the continuous part again provided the best fit when compared to the normal and gamma distributions as alternatives. The probability plot in Figure 60 illustrates the general conformance to a straight line. The corresponding plot for the gamma distribution (Figure 61) is not a straight line, indicating the gamma is not as good a fit for this data set. The distribution with estimated parameters is:

$$G(C) = 0.1472\ LN(C;-13.55,2.42) + 0.8528I(C)$$

where the terms are as previously defined. These parameter values result in an estimated mean value of 2.44×10^{-5} with a standard deviation of 4.55×10^{-4}.

The summary statistics at Four Mile Creek River Kilometer 5 and Wolf Creek River Kilometer 5 show the effect of the instream model embodied in SERATRA. First, the pesticide concentration is above the cutoff value longer near the Wolf Creek mouth (16.23%) than near the mouth of Four Mile Creek (14.72%). Second, the average concentration downstream in Wolf Creek is approximately five times smaller than that in Four Mile Creek. If the

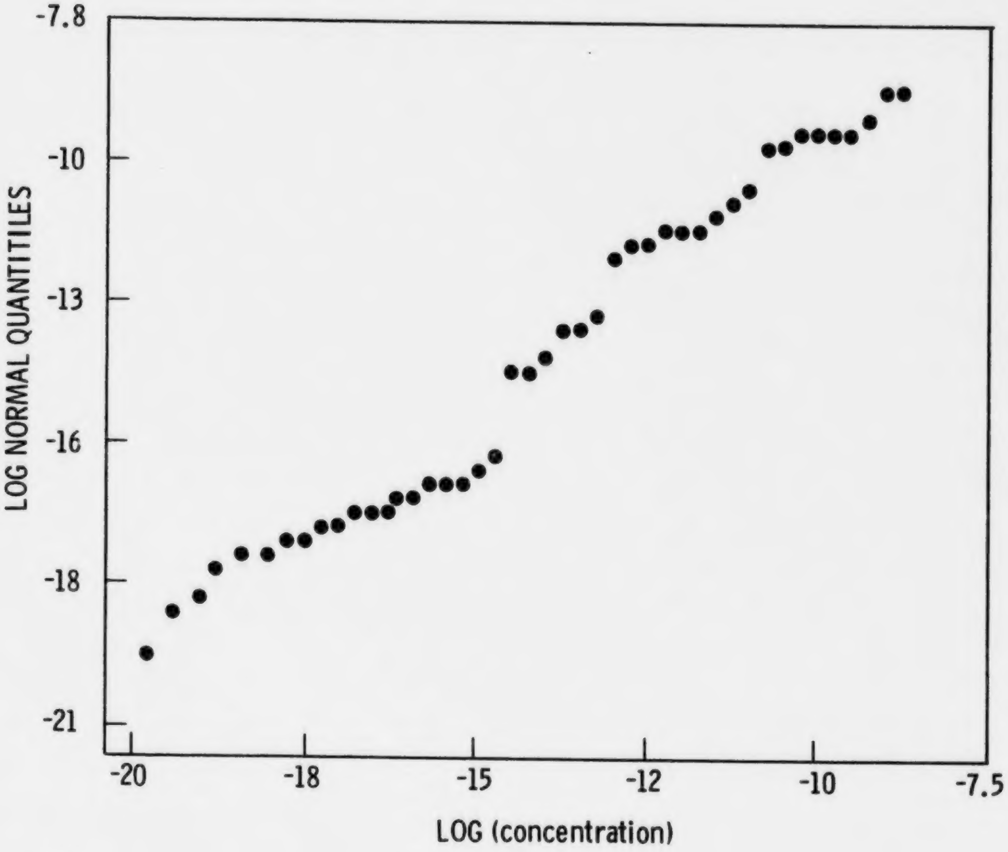


Figure 60. Log-normal probability plot for dissolved pesticide concentration at Four Mile Creek River kilometer 5 ($\mu = -13.55$, $\sigma = 2.42$)

comparison is made in log concentrations where the estimated distribution is normal, then it appears that the difference is mainly a shift in the mean value with the log variability approximately the same between these two locations.

The pesticide attached to particulates was also summarized using the mixed distribution analysis just described. The distributions of the simulated results for particulate pesticides (in kg/m^3) from ARM, at Four Mile Creek River Kilometer 5 and at Wolf Creek River Kilometer 5 were again a mixed distribution with the log-normal distribution as the continuous form. At stream-edge,

$$G(C) = 0.0017 \text{ LN } (C;-17.27,1.92) + 0.9983 \text{ I}(C)$$

at Four Mile Creek River Kilometer 5

$$G(C) = 0.1367 \text{ LN } (C;-17.34,2.88) + 0.8633 \text{ I}(C)$$

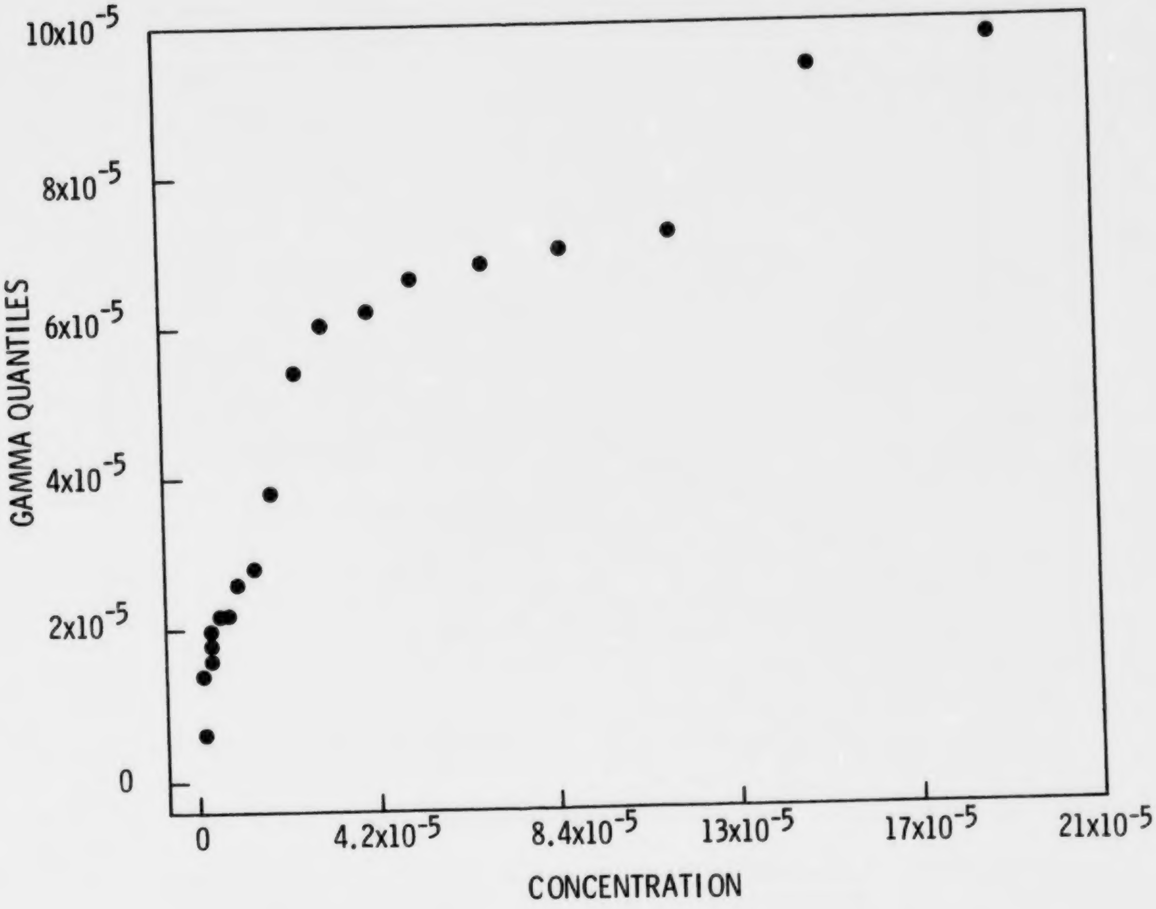


Figure 61. Gamma probability plot for dissoved pesticide concentration at Four Mile Creek River Kilometer 5 (α = 0.28, β = 1.7 x 10^4)

and at Wolf Creeek River Kilometer 5

$$G(C) = 0.0996\ LN\ (C;-19.70,2.55) + 0.9004\ I(C)$$

Particulate pesticide concentration levels were lower than the dissolved pesticide concentration as expected.

Total pesticide concentration (sum of dissolved and particulate pesticide concentrations) were similarly analyzed. The results are not presented as they are virtually identical to the dissolved case. Particulate pesticide concentrations do not significantly contribute, in this case, to the total concentration.

The distribution analysis was also applied to the dissolved pesticide concentration at stream-edge as simulated by the ARM model. The mixed distribution model with the log-normal as the continuous part again was an adequate fit. In this case the gamma distribution was a close competitor. The log-normal was selected to facilitiate the comparison with the SERATRA results. The estimated distribution is:

$$G(C) = 0.0707\ LN(C; -10.66, 2.45) + 0.9293\ I(C)$$

$$I(C) = \begin{cases} 1 & C \leq 2 \times 10^{-9} \\ 0 & C > 2 \times 10^{-9}. \end{cases}$$

In comparison with the instream results, the stream edge concentrations above the cutoff value were less than half as long (7.07%) and the concentration distribution was shifted to higher concentrations with no difference in the variability in log units. The average concentration based on the log-normal distribution was 4.72×10^{-4} with a standard deviation of 9.48×10^{-3}. The general effect of SERATRA on the pesticide distribution is to lengthen the time the concentration is above the cutoff value and to reduce the average concentration level.

The statistical summary of the pesticide concentrations from ARM and SERATRA has demonstrated that it is possible to describe the distribution with a mixed probability distribution with the continuous part being a log-normal distribution. The estimated parameters for this mixed distribution reflect the anticipated pesticide concentration changes expected when going from stream-edge, to instream, and instream further downstream. A severe limitation of this type of summary is the loss of all the time sequence history of the concentrations. In the present work no method was found to include duration of events in a distribution analysis.

The distribution analysis illustrates the feasibility of summarizing the pesticide concentration distribution at stream-edge and at selected instream locations. The summaries were shown to have the same mixed distribution form with only the values of the parameters in the distribution changing at each location. To simplify the methodology, the relationship among the parameters across locations must be determined. The case study illustrated the parameters changed in the direction intuitively expected. However, it is not possible to determine a quantitative relationship. A large number of case studies at different sites, each simulated under a variety of conditions, would be necessary to determine a quantitative relationship. The computational time required for each simulation may become excessive when a large number of simulations must be completed. A second limitation is related to the calibration procedures presently required for both the ARM and SERATRA models. If the calibration is unique to each site of application, then the simplified statistical methodology must be able to account for this. The severity of the problem can not be determined until more case studies are completed.

Additional study on a simplified statistical methodology must consider another question. What is the minimal information required concerning pesticide occurrence and duration for a useful risk assessment? An answer to the question along with a specific statistical summary procedure must be available before detailed studies of a simplified approach can be useful. Experience in applying the present CMRA Methodology will be useful in determining the information necessary for a risk assessment and in formulating an effective statistical summary for the information.

REFERENCES

Adams, R. T. and F. M. Kurisu. 1976. Simulation of Pesticide Movement on Small Agricultural Watersheds. EPA-600/3-76-077. U.S. Environmental Protection Agency, Washington, DC.

Baca, R. G., W. W. Waddel, C. R. Cole, A. Brandstetter and D. B. Cearlock. 1973. EXPLORE-I: A River Basin Water Quality Model. Submitted to U.S. Environmental Protection Agency. Pacific Northwest Laboratory, Richland, WA 99352.

Baker, J. L., H. P. Johnson, M. A. Borcherding, and W. R. Payne. 1979. "Nutrient and Pesticide Movement from Field to Stream: A Field Study." In Best Management Practices for Agriculture and Silviculture, Proceedings of the 1978 Cornell Agricultural Waste Management Conference. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Call, D., L. Brooke, and R. Kent. 1979. Estimates of No-Effect Concentration of Selected Pesticides in Freshwater Organisms. Third Quarterly Progress Report to EPA, 1 January through 31 March 1979. U.S. EPA Grant No. R-806196-01. University of Wisconsin, Superior, WI.

Crawford, N. H. and A. S. Donigian. 1973. Pesticide Transport and Runoff Model for Agricultural Lands. EPA-660-2-76-013, U.S. Environmental Protection Agency, Washington, DC.

Crawford, N. H. and R. K. Linsley. 1966. Digital Simulation in Hydrology: Stanford Wasteshed Model IV. Department of Civil Engineering, Technical Report No. 39, Stanford University, Stanford, California.

Dawson, G. W., M. W. Stradley, A. J. Schuckrow. 1974. Determination of Harmful Quantities and Rates of Penalty for Hazardous Substances. Prepared for the U.S. Environmental Protective Agency by Pacific Northwest Laboratory, Volume 3 - Appendices, Washington, DC.

Donigian, A. S. and N. H. Crawford. 1976. Modeling Pesticides and Nutrients on Agricultural Lands. EPA-600/2-76-043, U.S. Environmental Protection Agency, Washington, DC.

Donigian, A. S., D. C. Beyerlein, H. H. Davis and N. H. Crawford. 1977. Agricultural Runoff Management (ARM) Model Verision II: REfinement and Testing. EPA-600/3-77-098, U.S. Environmental Protection AGency, Washington, DC.

Donigian Jr., A. S., and H. H. DAvis, Jr. 1977. User's Manual for Agricultural Runoff Management (ARM) Model. EPA-600/3-78-080, U.S. Environmental Protection Agency, Washington, DC.

Donigian, A. S. and H. HJ. Davis. 1978. Agricultural Runoff Management (ARM) Model User's Manual: Versions I and II. EPA-600/3-78-080, U.S. Environmental Protection Agency, Washington, DC.

Eaton, J.G. 1973. "Recent Developments in the Use of Laboratory Bioassays to Determine "safe" Levels of Toxicants for Fish." In Bioassay Techniques an Environmental Chemistry. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Ellis, B. G., A. E. Erickson, A. R. Wolcott, M. Zabile and R. Leavitt. 1977. Pesticide Runoff Losses from Small Watersheds in Great Lakes Basin. EPA-600/3-77-112, U.S. Environmental Protection Agency, Washington, DC.

Environmental Protection Agency. 1972. Effects of Pesticides in Water - A Report to the States. PBB222-320, Prepared for Office of Water Resources Research by NTIS, U.S. Department of Commerce.

Environmental Protection Agency. 1978. Kepone Mitigation Project Report. Standards and Criteria, Office of Water and Hazardous Materials, U.S. Environmental Protection Agency, Washington, DC.

Environmental Protection Agency. 1979. "Water Quality Criteria." Federal Register, Vol. 44, No. 52, pp. 15296-15981, U.S. Environmental Protection Agency, Washington, DC.

Fread, D. L. 1973. "Technique for Implicit Dynamic Routing in Rivers with Major Tributaries," Water Resources Research, Vol. 9, No. 4, pp. 918-926.

Frere, M. H., C. A. Onstad and H. N. Holtan. 1976. Actmo, An Agricultural Chemical Transport Model. Agricultural Research Service, ARS-H-3, U.S. Department of Agriculture, Washington, DC.

Guenzi, W. D. (Ed.) 1974. Pesticides in Soil Water. Soil Science Society of America, Inc., Madison, WI.

Haan, C. T. 1977. Statistical Methods in Hydrology. Iowa State University Press, Ames, IA.

Herbicides Handbook of the Weed Science Society of America. 1970. Weed Science Society of America, 2nd Edition, pp. 80-83, W. F. Humphrey Press, Geneva, NY.

Jordan, G. L. 1978. "Environmental FActors and Soil Relationships Influencing the Activity of Acetauilidie Herbicides." Ph.D. Dissertation, University of Wisconsin, Madison, WI.

Laflen, J. M., J. L. Baker, R. O. Hartwig, W. F. Buchele and H. P. Johnson. 1976. "Soil and Water Loss from Conservation Tillage Systems." Transactions of the ASAE, 21/5:881-885.

Leendertse, J. J. 1970. A Water Quality Simulation Model for Well Mixed Estuaries and Coastal Seas, Principles of Computation, Volume I. RM-6230-RC, The Rand Corporation, Santa Monica, CA.

Leytham, K. M., and R. C. Johanson. 1979. Watershed Erosion and Sediment Transport Model. Submitted to the Environmental Protection Agency by Hydrocomp, Inc., Palo Alto, CA.

McElroy, A. D. et al. 1976. Loading Functions for Assessment of Water Pollution Nonpoint Sources. Midwest Research Institute, (PB-253 325).

Norton, W. R., L. A. Roesner, D. E. Evenson and J. R. Monser. 1974. "Computer Program Documentation for the Stream Quality Model, Qual-II." Water Resources Engineers, Inc., Walnut Creek, CA.

Oak Ridge National Laboratory. 1978. Proceedings of a Workshop on Evaluation of Models Used for the Environmental Assessment of Radionuclide Releases. CONF-770901, September 6-9, 1977, Gatlinburg, TN.

Olsen, A. R., and S. E. Wise. 1979. Frequency Analysis of Pesticide Concentrations for Risk Assessment. Submitted to U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y., P. A. Johanson, R. G. Baca and E. L. Hilty. 1976. Studies of Columbia River Water Quality - Development of Mathematical Models for Sediments and Radionuclide Transport Analysis. BNWL-B-452. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. and S. E. Wise. 1978. "Mathematical Modeling of Sediment and Contaminant Transport in the James River Estuary." Proceedings of the 26th Annual ASCE Hydraulic Division Specialty Conference on Verification of Mathematical and Physical Models in Hydraulic Engineering, pp. 303-310, College Park, MD, August 9-11, 1978.

Onishi, Y. 1979a. "Evaluation of Hazardous Substance Transport Modeling in Surface Waters." Proceedings of EPA National Workshop on Verification of Water Quality Models, West Point, NY, March 7-9, 1979.

Onishi, Y., D. L. Schreiber and R. B Codell. 1979b. "Mathematical Simulation of Sediment and Radionuclide Transport in the Clinch River, Tennessee." Proceedings of ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979. "Contaminants and Sediments," R. A. Baker (Ed.), Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Onishi, Y. and S. E. Wise. 1979c. Mathematical Model, SERATRA, for Sediment and Contaminant Transport in Rivers and its Application to Pesticide Transport in Four Mile and Wolf Creeks in Iowa. Submitted to the U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. and S. E. Wise. 1979d. User's Manual for the Instream Sediment-Contaminant Transport Model, SERATRA. Submitted to the U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. 1979e. User's Manual for EXPLORE-I: A River Basin Water Quality Model (Hydraulic Module Only). Submitted to the U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Roesner, L. A., et al. 1976. Agricultural Watershed Runoff Model for the Iowa-Cedar River Basins. Report for U.S. Environmental Protection Agency, Systems Development Branch, Washington, DC.

Sprague, J. B. 1969. "Measurement of Pollutant Toxicity to Fish: Bioassay Methods for Acute Toxicity." Water Research, 3:793-821, Pergamon Press, GREAT BRITAIN.

Stephan, C. E. 1977. "Methods for Calculating an LC50." In Aquatic Toxicology and Hazard Evaluation Proceedings of the Annual Symposium on Aquatic Toxicology (ASTM), Special Technical Publication 634:65-83, American Society for Testing and Material, Philadelphia, PA.

Stewart, B. A., D. A. Woolhiser, W. H. Wischmeier, J. H. Caro, and M. M. Frere. 1976. Control of Water Pollution for Cropland: Volume I - An Overview. Agricultural Research Service, U.S. Department of Agriculture, Washington, DC.

Water Quality Criteria. 1972. Committee on Water Quality Criteria, EPA-Re-73-033. U.S. Environmental Protection Agency, Washington, DC.

Wauchope, R. D. 1978. "The Pesticide Content of Surface Water Draining from Agricultural Fields - A Review." Journal of Environmental Quality, Vol. 7, No. 4.

Wuhrmann, K. 1952. "Concerning Some Principles of the Toxicology of Fish." Bull. Cent. Gelge. Docum. Eaux. (Fisheries Research Board of Canada Translation Series, No. 243.) No. 15:49.

Weed Science Society of America. 1979. Herbicide Handbook. Fourth Edition. Champaign, IL.

APPENDIX A

PROCEDURE FOR CMRA METHODOLOGY APPLICATION

Step-by-step instructions to use the CMRA Methodology will be described.

OVERLAND PESTICIDE MODELING

The first step in the CMRA Methodology is the application of ARM to the selected study area. The procedure to be followed is essentially the same as the five major steps outlined by Donigian and Davis (1977). These steps are discussed briefly below and have been slightly modified for use in this study.

Step 1: Data Collection and Analysis

Once the pesticide, application practice and study area have been selected, the input data for ARM must be collected and analyzed. These input or execution data basically consist of meteorologic data, such as precipitation, potential evapotranspiration, maximum-minimum air temperature, wind movement, dewpoint temperature and solar radiation. If snowmelt calculations are not required, only the first two types of meteorologic data are needed. Because ARM is a continuous simulation model, these data are required for the entire duration of the simulation time period. The length of this time period is primarily determined by statistical considerations to be discussed later as well as data availability and the required computation time.

Step 2: Preparation of Meteorologic Data and Model Input Sequence

This step consists of the construction of input data files for each type of meteorologic data. The procedures for constructing these files and their input formats have been described in detail by Donigian and Davis (1977).

Step 3: Parameter Evaluation

Several of the ARM model parameters can be evaluated directly without going through the calibration process. The types of information required to evaluate these parameters include topographic maps, soil maps, hydrologic/meteorologic studies, water quality studies, cropping pattern surveys, and data on pesticide application rates and modes. The specific parameters which can be evaluated in this manner and methods of evaluation have also been described by Donigian and Davis (1977).

Step 4: Model Calibration and Verification

Calibration is an iterative process of making computer runs and coefficient adjustments until simulated results match observed results. It is required for parameters which cannot be determined directly. The calibration process for the ARM model has been refined over several years of effort and is discussed in great detail by Donigian and Davis (1977).

Step 5: Generation of Runoff and Edge-of-Stream Sediment and Pesticide Loadings

Upon completion of the previous steps, the ARM model can be used to generate the runoff and sediment and pesticide loading information required as input to the instream modeling component of the methodology. This step basically involves obtaining historical meteorological data for a given time period or the selection of data which represent a specific sequence of storm events. Pesticide application times can be based on local conditions or selected arbitrarily. In the latter case, pesticide removal by runoff and erosion can be maximized by selecting pesticide application times several days to several weeks before major storm events. Pesticide application rates and modes and cropping patterns can be obtained from local information; if the pesticide being evaluated is new, application rates and modes can be obtained from the manufacturer.

The information generated in this step of the methodology is a time history of each of the following: runoff, sediment loading, pesticide dissolved in the runoff and pesticide attached to the sediment. Depending on the size and configuration of the watershed, this information is generated for each catchment individually or for the total watershed. The in-stream sediment and contaminant transport model, SERATRA (Onishi and Wise 1979a,b), requires the pesticide attached to each size fraction of sediment being modeled in the river system. However, ARM only simulates total sediment loading and total pesticide adsorbed to the sediment. Therefore, the ARM simulation results have to be modified prior to their input to SERATRA.

INSTREAM PESTICIDE MODELING

Instream pesticide modeling requires two computer models. EXPLORE-I (Baca et al. 1973; Onishi 1979) is used to obtain one-dimensional, unsteady distributions of discharge (or velocity) and depth in a receiving water body. Computed runoff is input to EXPLORE-I as a tributary contribution. SERATRA is used to simulate pesticide migration by solving both sediment and pesticide transport. SERATRA uses EXPLORE-I results and computed sediment and pesticide loading from overland as input data. Simulation results of pesticide distributions in a receiving stream are then statistically analyzed to be used for the pesticide risk assessment. Because of the lack of toxicological knowledge, only dissolved pesticide distributions are used for the risk assessment.

Step 1: Hydrodynamic Data Collection and Analysis:

Once the study area is selected, the input data for EXPLORE-I must be collected and analyzed. These data consist of channel geometry and the Manning's coefficient of the stream. If there is a dam in the study area, obtain the operational characteristics of the dam to be inputed to EXPLORE-I. Boundary conditions at the upstream and downstream ends and at tributary confluences must be specified. These boundary conditions may be time varying inflows or water surface elevations during the entire simulation period. Initial flow conditions must also be specified. The simulation period is the same as that used in the overland modeling component.

Step 2: Preparation of EXPLORE Input:

Assemble the input data outlined in Step 1 along with the runoff computed with ARM.

Step 3: EXPLORE-I Calibration and Verification:

EXPLORE-I must then be calibrated to match measured depth and velocity distributions by adjusting the Manning coefficient. If more than one set of measured data are available for different discharges, use the first set of observed data for calibration and the other set(s) of data for model verification.

Step 4: Production Run for Hydrodynamic Simulation:

Upon completion of above steps, run the EXPLORE-I model to obtain depth and velocity (or discharge) distributions.

Step 5: Sediment and Pesticide Data Collection and Analysis

Collect necessary input data of sediment and pesticide characteristics, as well as initial and boundary values of sediment and pesticide concentrations. Detailed information of SERATRA formulation, data need and modeling procedure is described in Onishi and Wise (1979a,b). Based on the analysis of data availability, decide whether to treat sediment as one bulk sediment, consequently one bulk particulate pesticide, or to divide the sediment into three sediment size fractions (or sediment types), resulting in three groups of particulate pesticide associated with each size fractions (or type) of sediment. The SERATRA user must realize that the discrepancy between actual and simulated sediment transport rates, hence also particulate pesticide transport rates will probably be large if only a single size fraction (or single type) of sediment is considered. The use of three size fractions (or types) is itself a compromise. If sediments are divided into three size fractions (or sediment types), then bulk sediment and pesticide loading computed by ARM must be separated into each size fraction (or sediment type), as described in Subsection 4.3.2. Care must be taken for selection of pesticide distribution coefficients.

Step 6: Preparation of SERATRA Input

Using data prepared under Step 5, and results obtained by ARM and EXPLORE-I, assemble the input data for SERATRA.

Step 7: SERATRA Calibration and Verification

With available field data, adjust model parameters, especially those associated with erosion and deposition of cohesive sediments (i.e., critical shear stresses and the erodibility coefficient) and dispersion coefficient, as model calibration. If there are additional field data for other flow conditions, use the sets of field data for model verification.

Step 8: Production Run for Sediment-Pesticide Transport Simulation

Upon completion of the previous steps, run SERATRA to obtain unsteady, vertical and longitudinal distributions of sediment and pesticide (both dissolved and particulate) concentrations. Sediment and pesticide conditions in the river bed will also be computed. Cross-sectionally averaged dissolved pesticide concentrations will then be used for the statistical analysis.

STATISTICAL ANALYSIS

The CMRA Methodology procedures require the summary of SERATRA output results of dissolved pesticide concentrations. Each of these areas are described in the order of their occurrence in the methodology.

Step 1: FRANCO (Olsen and Wise 1979) Analysis of SERATRA Instream Pesticide Concentration

The FRANCO program requires particular information to be available for a meaningful analysis (Olsen and Wise, 1979). The SERATRA model cutoff pesticide concentration value and the maximum pesticide concentration are needed. A time series plot of the data is helpful. An array of user specified concentration values, a similar array of duration values and a number of LC (lethal concentration) functions are needed to control the summary of the simulated pesticide concentrations. The LC functions are specified to provide the information needed for the risk assessment. The selection of these functions is discussed in the following risk assessment steps. The concentration and duration values are selected with consideration for both the risk assessment needs and the statistical requirements for providing detail on the frequency of occurrence and duration of specific pesticide concentrations.

RISK ASSESSMENT

Step 1: Lethality

Data must be located for pertinent aquatic species in response to the pesticide under investigation. These values should be stated as LC50 (median lethal concentration) or TLm (median tolerance limit) for a specific time interval such as 24-hr LC50. The minimum number of points required include the 24-, 48-, and 96-hr LC50 numbers, for each pesticide and species. Include the confidence limits around each point and any experimental conditions specifically indicated. Incipient LC50 values, when given, should also be recorded. Sources for such information include toxicological literature, the Office of Pesticide Programs, EPA files, and pesticide manufacturers. A reference list is included in the Appendix B and may be useful in obtaining these data.

If all values 24, 48, and 96-hr LC50 for the specific pesticide and aquatic species are available and there are no conflicting values, use the data as it is. Where conflicting data occur and can be traced to the conditions under which the tests were performed, use the results most similar to the field conditions being studied. For example, results may be given for temperatures of 7 and 20°C. The temperature most closely approximating an actual average stream temperature should be used.

(Optional) Standardize values from static bioassays of calculated concentrations to flow-through bioassays of measured concentrations by the following factors:

Static value x 0.71 approximates Flow-through values

Calculated concentrations x 0.77 approximates Measured values.

Frequently, data lists do not provide all necessary LC50 points. Use one of the following methods to extrapolate missing values in the data.

1. Find the slope between concentrations at the 24, 48, and 96-hr LC50 intervals for a genus or family related aquatic species subjected to the same pesticide to approximate the missing point or points. See Appendix B for a partial phylogenetic chart.

Example:(from dieldrin)	24-hr	48-hr	96-hr	LC50
Given: Lepomis macrochirus	5.5	3.4	2.8	ppb
Lepomis gibbosus	-	-	6.7	ppb

Lepomis macrochirus — Lepomis gibbosus

$$\text{Slope } \frac{2.8 - 3.4}{96 - 48} = \frac{-.6}{48} = -.0125 \qquad \frac{6.7 - C_{48}}{96 - 48} = -.0125$$

$$C_{48} = 7.3$$

$$\frac{3.4 - 5.5}{48 - 24} = \frac{-2.7}{24} = -.0875 \qquad \frac{7.3 - C_{24}}{48 - 24} = -.0875$$

$$C_{24} = 9.4$$

$$\frac{2.8 - 5.5}{96 - 24} = \frac{-2.7}{72} = -.0375 \qquad \frac{6.7 - C_{24}}{96 - 24} = -.0375$$

$$C_{24} = 9.4$$

Now concentration values for 24 and 48 hours have been generated and may be used to approximate experimental numbers.

2. Use the geometric mean of the toxicity slopes for other species of the same order exposed to the same pesticide. Calculate the missing values using these geometric mean values for 24, 48, and 96 hours.

3. Use the standardization factors suggested in the Federal Register (1978) to estimate 96-hr LC50 values. The reciprocals of these number can be used to derive data points for 24, 48, and 72 hours.

Given: 24-hr LC50: multiply by 0.66 to estimate 96-hr LC50
48-hr LC50: multiply by 0.81 to estimate 96-hr LC50
72-hr LC50: multiply by 0.92 to estimate 96-hr LC50
96-hr LC50: multiply by 1.52 to estimate 24-hr LC50
96-hr LC50: multiply by 1.23 to estimate 48-hr LC50
96-hr LC50: multiply by 1.09 to estimate 72-hr LC50

If the pesticide of interest has no toxicity data for the species, several alternatives remain to find data indicative of the probable toxicity trend. However, without experimental results, the accuracy of these estimates cannot be assumed.

1. Find the toxicity range of genus related species and use this range as the most likely to include the actual values. A geometric mean may be calculated, if desired, for computer handling.

2. For no genus related species, use family, then order, then class if necessary to obtain enough data to describe a toxicity range.

3. Use toxicity data from a related pesticide for the same species or at least the same genus to approximate toxicity if the two pesticides are known to cause similar biological effects.

Step 2: Sublethal Toxicity

Find the MATC (maximum acceptable toxicant concentration) range for the pesticide and aquatic species in question. If the range is specifically given in the literature, use it. Where chronic data is given and includes no effect levels, use the highest no effect level and the lowest chronic effects concentration to determine the MATC range.

Example: Highest concentration with no effect - 50 ppb
Lowest concentration with effects - 100 ppb

$$50 < \text{MATC} < 100 \text{ ppb}$$

A MATC range may be found for another species for the same pesticide. The next two steps describe the procedure to use this MATC value for deriving one for the species in question.

1. Calculate an application factor (AF) from the known MATC of the other species.

   MATC (other species)/96-hr LC50 (other species)
   = Application Factor Range

2. Use the AF to calculate the new MATC.

   AF range (from above) x 96-hr LC50 (of desired species)
   = MATC range (for desired species)

Alternatives may be used when no MATC ranges or chronic data can be obtained. These include the following:

1. Use an arbitrary AF based on the pesticide's known persistence and cumulative effects.

   a. If the pesticide is neither persistent nor cumulative in toxicity, use 0.05 as the AF for a 24 hr average or 0.1 for a temporary concentration level.

   b. If the chemical is known to have persistent and/or cumulative toxicity properties, use 0.01 for the 24 hr average or 0.05 for a temporary AF.

   2. Where a MATC range is given for the species for a related pesticide, the use of its derived AF may be a better estimate than an arbitrary AF.

The MATC range may be converted to a single concentration value for convenient computer manipulation. Either endpoint or a geometric mean are possible choices. The lowest value in the range (the highest no effect level) is preferred as the most conservative choice.

Step 3. Input to the FRANCO Model

The choice of curve formation depends on its intended use. FRANCO will determine the number of times a curve is exceeded, the duration of each exceedance event, the total time of exceedance, and the percentage of total time that the curve is exceeded as the fraction over SERATRA cutoff, i.e., total event time. Suggested curves are included below for each aquatic species being studied.

1. A SERATRA cutoff. This one is discussed in Chapter 4.

2. The MATC as one of the endpoints or the geometric mean. Use of both endpoints requires two curves (see Figure 13a).

3. The LC50-MATC conservative curve indicating the greatest chance for lethality (see Figure 13b).

4. The lethal curve least likely to indicate lethality (see Figure 13c).

5. The intermediate curve (see Figure 13d).

6. The MATC line from 96 hours to the end of the test period.

7. The LC50 or LC50-MATC line beyond 48 or 96 hours.

FRANCO accepts a maximum of six duration-concentration pairs of points to define each curve (function). Time is in hours and concentrations are expressed as Kg/m^3 (1×10^3 mg/l). Pair point choices are dictated by the selection of each curve. Each line segment must be defined by two points. For straight line sections such as the MATC, designation of two separate durations at the same concentration is required.

Step 4. Interpretation of Results

The Exceedance Summary produced by FRANCO lists the following values for each curve:

1. The number of times curve concentration levels were exceeded.

2. The total number of time steps.

3. The total percent of modeling time in which the curve was exceeded.

Additional information obtained by FRANCO is described in Section 4.2. Particular points of interest may include the highest concentration level reached, the time steps in which an event occurred, and the percentage of time steps lasting longer than some time d_x at Concentration C_x.

Results may be briefly summarized as illustrated in Figure A.1. Section A, below the MATC line, is presumed safe and is calculated as the percentage exceeding the MATC (sample curve 2 in Figure 13a) subtracted from 100%. Potential lethal and sublethal Section B, which includes lethality less than 50%, is calculated by subtracting the global exceedance determined from sample curve 4 (Figure 13c) from the MATC curve (sample curve 2). Section C measures lethality as exceedance of the LC50 curve. Sample curve 4 is used in this example. Sample curve 3 (Figure 13b) may be used instead if desired.

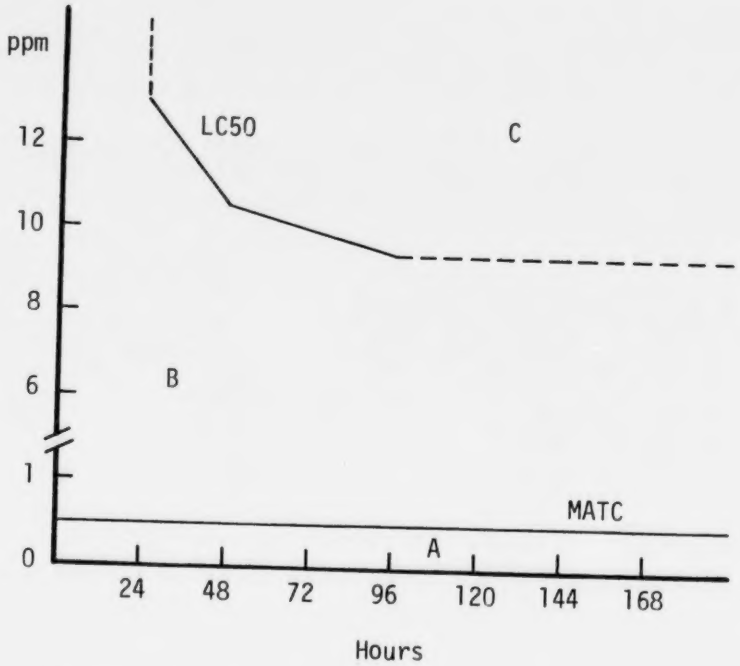


Figure A.1. Summary of global exceedance results.

REFERENCES

Baca, R. G., W. W. Waddel, C. R. Cole, A. Brandstetter and D. B. Cearlock. 1973. EXPLORE-I: A River Basin Water Quality Model. Submitted to U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA 99352

Donigian Jr., A. S., and H. H. Davis, Jr. 1977. Agricultural Runoff Management (ARM) Model User's Manual: Versions I and II. Submitted to U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens GA. Hydrcomp, Inc., Palo Alto, CA.

Olsen, A. R., and S. E. Wise. 1979. Frequency Analysis of Pesticide Concentrations for Risk Assessment. Submitted to U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. 1979. 1979 User's Manual for EXPLORE-I: A River Basin Water Quality Model (Hydraulic Module Only). Submitted to U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. and S. E. Wise. 1979a. Mathematical Model, SERATRA, for Sediment and Contaminant Transport in Rivers and its Application to Pesticide Transport in Four Mile and Wolf Creeks in Iowa. Submitted to U.S. Environmental Protection Agency. Battelle, Pacific Northwest Laboratories, Richland, WA.

Onishi, Y. and S. E. Wise. 1979b. User's Manual for the Instream Sediment-Contaminant Transport Model, SERATRA. Submitted to U.S. Environmental Protection Agency, Battelle, Pacific Northwest Laboratories, Richland, WA.

APPENDIX B

TOXICOLOGICAL PROPERTIES OF PESTICIDES

The following tables are divided into two sections. The first is a compilation of toxicity data on individual pesticides and the second is a listing of groups of related pesticides along with properties of persistence, solubility, and Kd values.

Table B.1 lists pesticides by their common generic names and functions. Several trade names are included to help identify the pesticide, but the use of such trade names is not intended as an endorsement of the product. The table has been divided into the taxonomic classes of fish, crustaceans, and insects. While the risk assessment procedure of the CMRA Methodology is not sufficiently sophisticated to assess the toxicological risk to invertebrates, they have been included for toxicity data comparison. A phylogenetic chart shown in Figure B.1 will help identify the relationships between common fish species and may be referred to during the assessment process. The list in Table B.2 identifies the scientific names of common fish.

The individual pesticide tables include information on lethality as 24-, 48-, and 96-hr LC50 concentrations, MATC ranges, and other acute or chronic effects. Occasionally, experimental conditions will be noted. All values are given in mg/l (ppm), and no attempt has been made to judge them for accuracy or standardize them to flow-though bioassays of measured concentration.

The reference bibliography is located at the end of this appendix. Not all citations are from the original articles. Further search for the original article is recommended for a better perception of the bioassay techniques and water conditions used.

Table B.3 divides many pesticides into chemical classes and lists solubility, Kd, soil and water persistence for them. Soil persistence is frequently listed as a half-life value (T/2). Water persistence values listed as percentages should be interpreted as percent remaining effective after the given length of time. The chemical family names used here include organochlorines, organophosphates, carbamates, phenylamides, phenoxyalkanoates, triazines, and a miscellaneous class. While chemically related compounds usually exhibit similar properties, individual members may display wide variation. Therefore, the generalizations stated below may not be applicable to all pesticides in the group.

Organochlorines

Chlorinated hydrocarbons, cyclodienes, and other oxygenated chlorine compounds are grouped in this category. These insecticides are persistent and most are rapidly assimilated by organisms in contact with them. Most are only very slightly soluble in water; typically less than 1 ppm will dissolve. Their high affinity for and solubility in lipids is the basis for their bioconcentration in the fats of an organism. Because of their low water solubility, they are highly immobile in soils where they are held and inactivated mostly by the soil organic component.

Most of the organochlorines are very persistent with half-lives of several years. Their degradation in soils takes place at a slow rate but can occur by microbial metabolism, photodecomposition, and by chemical reaction. Degradation products of some of these are also insecticidal, prolonging their effect in the soil. Volatilization may be a signficant method of removal from both soil and water. These pesticides should leach only a very short distance through the soil profile.

Entrance into the aquatic system from agricultural lands occurs almost entirely through soil erosion and watershed runoff. Once in the stream most will settle to the bottom and be associated with the sediment where it will equilibrate with the small dissolved fraction. Persistence in static water bodies is very long and toxaphene has been shown to be active after ten years.

Organochlorines as a group are highly toxic to aquatic animals and manifest an acute median lethal concentration less than 0.5 ppm for almost all of them. Biomagnification by uptake through the food chain or direct adsorption from water is not likely to occur in moving river communities (Macek, 1977). However, where biomagnification and transfer does occur, resistances to a pesticide by a species may have drastic effects on the next trophic level.

Organophosphates

Organophosphates have demonstrated toxic effects to a variety of organisms and have been used not only as insecticides, but also as herbicides and fungicides. Their advantage over organochlorines lies in their transience in the soil with residues disappearing between crop seasons.

The properties of organophosphates often cover a wide range. As a group they are slightly soluble in water but can vary from less than 1 ppm (Dioxathion) to 13% (Trichlorfon) or more. Movement in soils is related to their solubilities with the most mobile usually being the most soluble. However, they tend to adsorb strongly to soils and are seldom leached below the surface.

Vapor pressures for this group exceed the organochlorines and they are readily susceptible to microbial and chemical degradation. The rate of degradation rises with increases in soil moisture, temperature, and acidity; with hydrolysis; oxidation; and volatility contributing to the low stability. Under moderate conditions organophosphates remain in soil no more than several months though parathion has been detected in sandy loam for up to 16 years (Guenzi, 1974).

Most aquatic contamination will result from runoff entering the watershed. Organophosphates tend to hydrolyze readily and have a comparatively short half-life in water. Prior to their degradation they are highly toxic to aquatic animals, several compounds are responsible for lethal effects to crustaceans around the 0.001 ppm level.

Carbamates

Carbamate compounds have been divided into the methyl carbamates, a thio- and dithio- group and the carbanilates and are effective as insecticides, fungicides, and herbicides. Insecticides act by contact or ingestion as competitive inhibitors of cholinesterase. Fungicides are useful in controlling foliar disease in agricultural crops. Herbicides are effective in preemergence application. Most methyl carbamates have insecticidal activity and most phenyl carbamates are herbicides. Thio- and dithiocarbamates are used as herbicides and fungicides. Carbamates have a relatively short residual life in soils and are readily degraded by most nontarget organism.

Carbamate compounds are somewhat volatile and most are broken down rather quickly by microbial and chemical degradation. They do not sorb strongly to soils and are easily leached. The carbanilates, however, are relatively immobile. Once in the water, they are quickly broken down with a significant reduction within one week. Most are moderately toxic to fish and very toxic to crustaceans.

Phenylamides

Amines and anilines, the nitroanilines, and the ureas comprise this group. Alternative names for these chemicals are the acetamides, acylanilides, toludines, and phenylureas, among others. Nearly all of these have herbicidal action and are metabolized similarly.

These pesticides show moderate soil persistence with significant microbial degradation. None are very soluble, and the nitroanilines are particularly insoluble (1 ppm or less in water). Several are somewhat volatile and their adsorption is directly related to the amount of organic matter. The nitroanilines are fairly immobile in the soils but the ureas, amides, and anilines do not sorb strongly and desorb rapidly. Toxicity of this category to aquatic animals is low.

Phenoxyalkanoates

This group of herbicides also exhibits low toxicity to aquatic animals. The phenoxy compounds are not readily adsorbed to clay minerals but will sorb in limited amounts to organic matter. They are slightly soluble and are easily leached. Their persistence in soils depends on soil water content usually ranging from one to six months.

Triazines

Triazines and triazoles are largely nonvolatile herbicides. Their wide range in persistence from two weeks to more than a year depends on soil type, soil moisture, and application amount. Adsorption, which is readily reversible, depends on soil composition, moisture, pH, and temperature. Some are moderately mobile while others demonstrate little leaching or lateral movement. Toxicity of these pesticides is low for fish and may be moderate to invertebrates.

Miscellaneous Pesticides

Included among the miscellaneous are such groups as the aliphatic and benzoic acids, the dipyridyls, nitrophenols, phthalimides, pyridines, and the uracils.

TABLE B.1. PESTICIDE EFFECT ON FISH AND CRUSTACEANS (ACUTE TOXICITY = mg/l).

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
ACROLEIN	FISH						
Aquatic herbicide	Salmo gairdneri	0.140					Pimentel 1971
(Bacteriocide)	Salmo trutta	0.046					Burdick et al. 1964
	Cyprinus carpio					Killed at 1-2 ppm	Herbicide Handbook 1970
	Pimephales promelas				>0.011 <0.042	ILC50-0.084	Macek et al. 1976
	Rasbora heteromorpha	0.14	0.16				Alabaster 1969
	Lepomis macrochirus	0.079					Burdick et al. 1964
	CRUSTACEANS						
	Daphnia magna		0.057		>0.017 <0.034		Macek et al. 1976
ALACHLOR	FISH						
Herbicide	Salmo gairdneri			2.3			Monsanto
(Lasso)	Ictalurus sp.			6.5			Monsanto
	Pimephales promelas	8.7	5.8	4.4	>0.51 <1.0		Call et al. 1979
	Lepomis macrochirus			13.4			Monsanto
	CRUSTACEANS						
	Crayfish			19.5			Herbicide Handbook 1979
ALDRIN	FISH						
Insecticide	Oncorhynchus kisutch		0.061	0.046		72 hr LC50-0.0486	Katz 1961
	Oncorhynchus tschawytscha	0.0124	0.0106	0.0075		72 hr LC50-0.0087	Katz 1961
	Salmo gairdneri	0.0424	0.0239	0.0177		72 hr LC50-0.0203	Katz 1961
	Carassius auratus			0.028		240 hr LC50-0.020	Henderson et al. 1959
	Pimephales promelas			0.028			Henderson et al. 1959
	Poecilia reticulata			0.033			Henderson et al. 1959
	Gasterosteus aculeatus		0.0483	0.0398		72 hr LC50-0.0415	Katz 1961
	Leopmis cyanellus			0.0085			QCW 1976
	Lepomis macrochirus	0.0096	0.0074	0.0052			Henderson et al 1959
	CRUSTACEANS						
	Daphnia magna	0.030	0.0292 (50 hr)				Sanders & Cope 1966
	Daphnia pulex		0.028				Sanders & Cope 1966
	Simocephalus serrulatus		0.023				Sanders & Cope 1966
	Asellus brevicaudus			0.008			Sanders 1972
	Gammarus lacustris	45	12	8			Sanders 1969
	Palaemonetes kadiakensis			0.050			Sanders 1972
	INSECTS						
	Ephemerella grandis			0.0089			Gaufin et al. 1965
	Pteronarcys californica	0.030	0.008	0.013			Sanders & Cope 1968
				0.180		30 day LC50-0.0025	Jensen & Gaufin 1966
	Acroneuria pacifica			0.200		30 day LC50-0.022	Jensen & Gaufin 1966
ALLETHRIN	FISH						
Insecticide	Salmo gairdneri	0.020	0.019	0.019			Cope 1965b
	Lepomis macrochirus			0.056			WQC 1972

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
ALLETHRIN (contd)	CRUSTACEANS						
	Daphnia pulex		0.021				Sanders & Cope, 1966
	Simocephalus serrulatus		0.056				Sanders & Cope, 1966
	Gammarus fasciatus			0.008			Sanders 1969
	Gammarus lacustris	0.038	0.020	0.011			Sanders 1969
	INSECTS						
	Pteronarcys californica	0.009	0.0056	0.0021			Cope, 1965b
AMITROLE Herbicide (Aminotriazole)	FISH						
	Oncorhynchus kisutch		325				Bond et al. 1960
	Lepomis macrochirus		>100				Sanders 1970
	Rasbora heteromorpha	1950	1350				Alabaster 1969
	CRUSTACEANS						
	Daphnia magna		30				Sanders 1970
	Cypridopsis vidia		32				Sanders 1970
	Asellus brevicaudus		>100				Sanders 1970
	Gammarus fasciatus		>100				Sanders 1970
	Palaemonetes kadiakensis		>100				Sanders 1970
	Orconectes nais		>100				Sanders 1970
ATRAZINE Herbicide	FISH						
	Salvelinus fontinalis				>0.21 <0.52	ICL50-4.9	Macek et al. 1976
	Pimephales promelas				>0.06 <0.12	ILC50-15	Macek et al. 1976
	Lepomis macrochirus				>0.10 <0.50	ICL50-6.7	Macek et al. 1976
	CRUSTACEANS						
	Daphnia magna		6.9		>0.14 <0.25		Macek et al. 1976
	Gammarus fasciatus		5.7		>0.06 <0.14		Macek et al. 1976
	INSECTS						
	Chironomus tentans		0.72		>0.11 <0.23		Macek et al. 1976
AZINPHOS-METHYL Insecticide Acaricide	FISH						
	Oncorhynchus kisutch	0.007	0.005	0.0042		72 hr LC50-0.0048	Katz 1961
				0.017			Macek & McAllister 1970
	Oncorhynchus tschawytscha	0.0068	0.0062	0.0043		72 hr LC50-0.0043	Katz 1961
	Salmo gairdneri	0.0047	0.0038	0.0032			Katz 1961
				0.014			Macek & McAllister 1970
	Salmo trutta			0.004			Macek & McAllister 1970
	Carassius auratus			4.27			Macek & McAllister 1970
	Cyprinus carpio			0.695			Macek & McAllister 1970
	Pimephales promelas			0.235			Macek & McAllister 1970
					>0.33 <0.51		McKim 1977
	Ictalurus melas			3.5			Macek & McAllister 1970
	Ictalurus punctatus			3.290			Macek & McAllister 1970
	Lepomis macrochirus			0.022			Macek & McAllister 1970
	Lepomis microlophus			0.052			Macek & McAllister 1970
	Micropterus salmoides			0.005			Macek & McAllister 1970
	Perca flavescens			0.013			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
AZINPHOS-METHYL (contd)	CRUSTACEANS						
	Daphnia magna		0.0002				Pimentel 1971
	Daphnia pulex		0.0032				Pimentel 1971
	Asellus brevicaudus			0.021			Sanders 1972
	Gammarus fasciatus			0.00010			Sanders 1972
	Gammarus lacustris	0.00056	0.00025	0.00015			Sanders 1972
	Gammarus pseudolimneaus					30 day-no effect-0.0001	WQC 1972
	Paleomonetes kadiakensis					5 day LC50-0.0012 20 day LC50-0.00016	Sanders 1972 Sanders 1972
	INSECTS						
	Ephemerella subvaria					30 day LC50-0.0045	WQC 1972
	Ophigomphus rupinsulensis			0.012		30 day LC50-0.0022	WQC 1972
	Pteronarcys californica	0.025	0.008	0.0015			Sanders & Cope 1968
				0.0046		30 day LC50-0.0013	Jensen & Gaufin 1966
	Pteronarcys dorsata			0.0121		30 day LC50-0.0049	WQC 1972
	Acroneuria lycorias					30 day LC50-0.0015	WQC 1972
	Acroneuria pacifica			0.0020		30 day LC50-0.00024	Jensen & Gaufin 1966
	Hydropsyche bettoni					30 day LC50-0.0074	WQC 1972
BROMACIL Herbicide	FISH						
	Salmo gairdneri		75-80	100			Sanborn et al. 1977
	Pimephales promelas		75-80	100			Sanborn et al. 1977
CAPTAN Fungicide	FISH						
	Salvelinus fontinalis			0.034	>0.0075 <0.018		Hermanutz et al. 1973
	Pimephales promelas			0.065	>0.0165 <0.0395		Hermanutz et al. 1973
	Lepomis macrochirus			0.072	>0.0187 <0.0446		Hermanutz et al. 1973
CARBARYL Insecticide (Sevin®)	FISH						
	Oncorhynchus kisutch	1.33	0.997	0.997			Katz 1961
				0.764			Macek & McAllister 1970
	Salmo gairdneri		1.60	1.35		72 hr LC50-1.35	Katz 1961
				4.34			Macek & McAllister 1970
	Salmo trutta			1.95			Macek & McAllister 1970
	Carassius auratus			13.2			Macek & McAllister 1970
	Pimephales promelas			14.6			Macek & McAllister 1970
				9.0	>0.21 <0.68	6 months-chronic effects-0.68	Carlson 1971
	Ictalurus melas			20			Macek & McAllister 1970
	Ictalurus puntatus			15.8			Macek & McAllister 1970
	Gasterosteus aculeatus						Cope 1965a
		19	16.625	3.990		72 hr LC50-6.175	Katz 1961
	Lepomis macrochirus	6.7					Johnson 1968
		3.4	2.5	2.0			Cope 1965b
				6.76			Macek & McAllister 1970
	Lepomis microlophus	3.5	2.0				Cope 1963
				11.2			Macek & McAllister 1970
	Micropterus salmoides			6.4			Macek & McAllister 1970
	Perca flavescens			0.745			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
CARBARYL (contd)	CRUSTACEANS						
	Daphnia magna					63 day-no effect-.005	WQC 1972
	Daphnia pulex		0.0064				Sanders & Cope 1966
	Simocephalus serrulatus		0.0076				Sanders and Cope 1966
	Asellus brevicaudus			0.240			Sanders & Cope 1966
	Gammarus fasciatus			0.26			Sanders 1972
	Gammarus lacustris	0.040	0.022	0.16			Sanders 1969
	Palaemonetes kadiakensis			0.0056			Sanders 1972
	Orconectes nais			0.0086			Sanders 1972
	INSECTS						
	Pteronarcys californica	0.030	0.013	0.0048			Cope 1965b
	Pteronarcys dorsata					30 day LC50-0.023	WQC 1972
	Pteronarcella badia	0.0050	0.0036	0.0017			Sanders & Cope 1968
	Acroneuria lycorias					30 day LC50-0.0022	WQC 1972
	Claassenia sabulosa	0.012	0.0068	0.0056			Sanders & Cope 1968
	Hydropsyche bettoni					30 day LC50-0.0027	WQC 1972
CHLORDANE Insecticide	FISH						
	Oncorhynchus kisutch	0.100	0.086	0.056		72 hr LC50-0.082	Katz 1961
	Oncorhynchus tschawytscha	0.059	0.059	0.057		72 hr LC50-0.057	Katz 1961
	Salmo gairdneri	0.022	0.010	0.0078			Cope 1965b
		0.056	0.044	0.044			Katz 1961
	Salvelinus fontinalis	0.125	0.102	0.047		166 hr LC50-0.025	Cardwell et al. 1977
		(27.2 hr)	(46 hr)				
	Esox lucius	>0.005					Cardwell et al. 1977
	Carassius auratus			0.082			Henderson et al. 1959
	Cyprinus carpio		1.16				Cardwell et al. 1977
	Pimephales promelas		0.0534	0.0369		192 hr IC-0.032	Cardwell et al. 1977
			(45 hr)				
				0.052			Henderson et al. 1959
	Ictalurus punctatus			0.500			Cardwell et al. 1977
	Poecilia reticulata			0.190			Henderson et al. 1959
	Gasterosteus aculeatus	0.118	0.118	0.090		72 hr LC50-0.090	Katz 1961
	Lepomis macrochirus	0.058	0.049	0.040			Cope 1965b
			0.121	0.059			Cardwell et al. 1977
	CRUSTACEANS						
	Daphnia magna			0.0284-0.0352			Cardwell et al. 1977
	Daphnia pulex		0.029				Sanders & Cope 1966
	Simocephalus serrulatus		0.024				Sanders & Cope 1966
			0.055				Cardwell et al. 1977
	Cyclops strenuus	1.0				Lethal threshold	Cardwell et al. 1977
	Asellus aquaticus	0.050				Lethal threshold	Cardwell et al. 1977
	Hyalella azteca			0.097			Cardwell et al. 1977
	Gammarus fasciatus			0.040			Sanders 1972
	Gammarus lacustris	0.160	0.080	0.026			Sanders 1969
	Palaemonetes kadiakensis			0.004		120 hr LC50-0.0025	Sanders 1972
	Cambarus affinis	1.0				Lethal threshold	Cardwell et al. 1977

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
CHLORONITROPHENYL DIMETHYL PHOSPHOROTHIOATE Insecticide (Chlorothion®)	INSECTS						
	Pteronarcys californica	0.170	0.055	0.015			Cope 1965b
	Hydropsyche sp.					34 hr LT50-1.65	Cardwell et al. 1977
	Chironomus sp.					8 hr LT50-0.015	Cardwell et al. 1977
	FISH						
	Carassius auratus	2.6	2.4	2.3			Pickering et al. 1962
	Pimephales promelas	4.9	2.9	2.8			Pickering et al. 1962
	Poecilia reticulata	2.3	2.0	1.2			Pickering et al. 1962
	Lepomis macrochirus	1.8	0.78	0.71			Pickering et al. 1962
	CRUSTACEAN						
	Daphnia magna		0.0045				WQC 1972
CHLORPYRIFOS Insecticide (Dursban®)	FISH						
	Salmo gairdneri	0.53-0.550					Pimentel 1971
	Notemigonus crypoleucas					36 hr LC50-0.35-.125	Ferguson et al. 1966
	Gambusia affinis					36 hr LC50-.215-.595	Ferguson et al. 1966
	Lepomis cyanellus					36 hr LC50-.023-.125	Ferguson et al. 1966
	Lepomis macrochirus			0.0036			Macek et al. 1972
	CRUSTACEANS						
	Gammarus fasciatus			0.00032			Sanders 1972
	Gammarus lacustris	0.00076	0.00040	0.00011			Sanders 1969
	INSECTS						
	Pteronarcella badia	0.0042	0.0018	0.00038			Sanders & Cope 1968
	Pteronarcys. californica	0.050	0.018	0.010			Sanders & Cope 1968
	Claassenia sabulosa	0.0082	0.0018	0.00057			Sanders & Cope 1968
COUMAPHOS Insecticide (Co-Ral®)	FISH						
	Oncorhynchus kisutch	22	20	15		72 hr LC50-18	Katz 1961
	Salmo gairdneri		1.80	1.50			Katz 1961
	Carassius auratus			>18.0			Pickering et al. 1962
	Pimephales promelas			18.0			Henderson et al. 1959
	Poecilia reticulata	>10	2.8	0.56			Pickering et al. 1962
	Gasterosteus aculeatus		2.25	1.86		72 hr LC50-1.86	Katz 1961
	Lepomis macrochirus			0.18			Katz 1961
	CRUSTACEANS						
	Daphnia magna		0.001				WQC 1972
	Gammarus fasciatus			0.00015			Sanders 1972
	Gammarus lacustris	0.00032	0.00014	0.000074			Sanders 1969
	INSECTS						
	Hexagenia sp.	0.430					Carlson 1966
	Hydropsyche sp.	0.005					Carlson 1966

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
CROTOXYPHOS Insecticide (Ciodrin®)	FISH						
	Salmo gairdneri			0.055			WQC 1972
	Ictalurus punctatus			2.5			WQC 1972
	Lepomis macrochirus			0.250			WQC 1972
	Micropterus salmoides			1.10			WQC 1972
	CRUSTACEANS						
	Gammarus fasciatus			0.011			Sanders 1972
	Gammarus lacustris	0.049	0.029	0.015			Sanders 1969
2,4-D Herbicide	FISH						
	Oncorhynchus kisutch			<1		BEE	McKim et al. 1975
				10		IOE	McKim 1975
	Salmo gairdneri		1.1			PGBE	Sanders 1970
				<1		BEE	McKim 1975
				10		IOE	McKim 1975
	Cyprinus carpio			96.5			JWPCF 1978
	Pimephales promelas			5.6	>0.3<1.5	BEE	Mount & Stephan 1967
	Gambusia affinis	0.91-1.7				BEE	McKim et al. 1975
	Poecilia reticulata			70.7			Brungs 1978
	Lepomis gibbosus			94.6			Brungs 1978
	Lepomis macrochirus		0.9			PGBE	Cope 1965a
		10.0	10.0			BEE	Davis & Hughes
	CRUSTACEANS						
	Daphnia magna		0.10			PGBE	Sanders 1970
			5.6			BEE	Sanders 1970
			4.0			Dimethylamine salts	Sanders 1970
			>100			Acid	Sanders 1970
	Daphnia pulex		3.2			PGBE	Cope 1965a
	Simocephalus serrulatus		4.9			PGBE	Cope 1965a
	Cypridopsis vidua		0.32			PGBE	Sanders 1970
			1.8			BEE	Sanders 1970
			8.0			Dimethylamine salts	Sanders 1970
	Asellus brevicaudus		2.2			PGBE	Sanders 1970
			3.2			BEE	Sanders 1970
			>100			Dimethylamine salts	Sanders 1970
	Palaemonetes kadiakensis		2.7			PGBE	Sanders 1970
			1.4			BEE	Sanders 1970
			>100			Dimethylamine salt	Sanders 1970
	Orconectes nais		0.90			PGBE	Sanders 1970
			1.1			BEE	Sanders 1970
			>100			Dimethylamine salt	Sanders 1970
	Gammarus fasciatus	4.1	2.6	2.5		PGBE	Sanders 1970
		6.5	5.9	5.9		BEE	Sanders 1970
			>100			Dimethylamine salt	Sanders 1970
			3.2			Acid	Sanders 1970
	Gammarus lacustris	2.1	1.8	1.6		PGBE	Sanders 1969
		1.4	0.76	0.44		BEE	Sanders 1969
		6.8	4.6	2.4		IOE	Sanders 1969
	INSECTS						
	Pteronarcys californica	8.5	1.8	1.6		BEE	Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DALAPON Herbicide	FISH						
	Oncorhynchus kisutch		340				Bond et al. 1960
	Salmo gairdneri	340	210				Alabaster 1969
	Carassius auratus					24 hr LC0-100	Herbicide Handbook 1970
						24 hr LC100-500	Herbicide Handbook 1970
	Pimephales promelas	420, 440	350, 410	290, 390			Surber & Pickering 1962
	Lepomis macrochirus	115	115	105			Cope 1965b
		480, 510	440	290, 440			Surber & Pickering 1962
	CRUSTACEANS						
	Daphnia magna		6.0				Pimentel 1971
	Daphnia pulex		11.0				Sanders & Cope 1966
	Simocephalus serrulatus		16.0				Sanders & Cope 1966
	INSECTS						
	Pteronarcys californica			>100			Sanders & Cope 1968
DDT Insecticide	FISH						
	Oncorhynchus kisutch	0.066	0.046	0.044		72 hr LC50-.044	Katz 1961
				0.004			Macek & McAllister 1970
	Oncorhynchus tschawytscha	0.038	0.017	0.0115		72 hr LC50-.044	Katz 1961
	Salmo gairdneri			0.007		15 day LC50-.00026	Macek & McAllister 1970
	Salmo trutta			0.002			Macek & McAllister 1970
	Salvelinus fontinalis					36 hr LC50-.0323	Johnson 1968
	Carassius auratus			0.021			Macek & McAllister 1970
	Pimephales promelas			0.019			Macek & McAllister 1970
					0.0004		Jarvinen 1976
	Ictalurus melas			0.005			Macek & McAllister 1970
	Ictalurus punctatus			0.016			Macek & McAllister 1970
	Gambusia affinis	0.500				72 hr LC50-.010	Johnson 1968
	Poecilia reticulata			0.043			Henderson et al. 1959
	Gasterosteus aculeatus	0.022	0.021	0.018		72 hr LC50-18.5	Katz 1961
	Lepomis macrochirus			0.008			Macek & McAllister 1970
	Lepomis microlophus			0.005			Macek & McAllister 1970
	Micropterа salmoides			0.002			Macek & McAllister 1970
	Perca flavescens			0.009			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia magna			0.001			Sanders 1972
	Daphnia pulex		0.00036				Sanders & Cope 1966
	Simocephalus serralatus		0.0025				Sanders & Cope 1966
	Asellus brevicaudus			0.004			Sanders 1972
	Gammarus fasciatus			0.0008			Sanders 1972
	Gammarus lacustris	0.0047	0.0021	0.001			Sanders 1969
	Palaemonetes kadiakensis			0.0023			Sanders 1972
	Orconectes nais			0.00024			Sanders 1972
	INSECTS						
	Pteronarcella badia	0.012	0.009	0.0019			Sanders & Cope 1968
	Pteronarcys californica	0.041	0.019	0.007			Sanders & Cope 1968
	Claassenia sabulosa	0.016	0.0064	0.0035			Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DEMETON Insecticide Acaricide (Systox®)	FISH						
	Carassius auratus	12	12	12			Pickering et al. 1962
	Pimephales promelas	3.6	3.6	2.9			Pickering et al. 1962
				3.6-4.2			Henderson et al. 1958
	Poecilia reticulata	0.70	0.70	0.66			Pickering et al. 1962
	Lepomis macrochirus	0.18	0.11	0.11			Pickering et al. 1962
	CRUSTACEANS						
	Gammarus fasciatus			0.027			Sanders 1972
DIAZINON Insecticide	FISH						
	Salmo gairdneri	0.380	0.170	0.090			Cope 1965b
	Lepomis macrochirus	0.052	0.030	0.022			Cope 1965b
				0.48			Allison & Hermanutz, 1977
	CRUSTACEANS						
	Daphnia magna		0.0043 (50 hr)				Sanders & Cope 1966
	Daphnia pulex		0.0009				Sanders & Cope 1966
	Simocephalus serrulatus		0.0018				Sanders & Cope 1966
	Gammarus lacustris	0.80	0.50	0.20			Sanders 1969
	Gammarus pseudolimneaus					30 day LC50-0.00027	WQC 1973
	INSECTS						
	Ephemerella subvaria					30 day LC50-0.00105	WQC 1972
	Ophiogomphus rupinsulensis					30 day LC50-0.0022	WQC 1972
	Pteronarcys californica	0.155	0.060	0.025			Sanders & Cope 1968
	Pteronarcys dorsata					30 day LC50-0.0046	WQC 1972
	Acroneuria lycorias			0.0017		30 day LC50-0.00125	WQC 1972
	Hydropsyche bettoni					30 day LC50-0.00354	WQC 1972
DICAMBA Herbicide (Banvel®)	FISH						
	Oncorhynchus kisutch	151					Pimentel 1971
	Salmo gairdneri	35	35	28			Herbicide Handbook 1970
	Cyprinus carpio	659	465				Herbicide Handbook 1970
	Lepomis macrochirus	130	40	23			Herbicide Handbook 1970
	CRUSTACEANS						
	Daphnia magna		>100				Sanders 1970
	Cypridopsis vidua		>100				Sanders 1970
	Asellus brevicaudus		>100				Sanders 1970
	Gammarus fasciatus		>100				Sanders 1970
	Gammarus lacustris	10	5.8	3.9			Sanders 1969
	Palaemonetes kadiakensis		>100				Sanders 1970
	Orconectes nais		>100				Sanders 1970
DICHLOBENIL Herbicide (Casoron®)	FISH						
	Salmo gairdneri	23	20,22	18			Cope 1965b
	Rasbora heteromopha	120	100				Alabaster 1969
	Lepomis gibbosus					LC50-10 to 20	Herbicide Handbook 1970
	Lepomis macrochirus	22	20	10			Cope 1965b
		17		14.7			Wilson & Bond 1969
		37	30				Hughs & Davis 1962

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DICHLOBENIL (contd)	Lepomis microlophus	>20					Cope 1963
	Micropterus salmoides	15		12.5			Wilson & Bond 1969
	CRUSTACEANS						
	Daphnia magna		10				Sanders 1970
	Daphnia pulex		3.7				Sanders & Cope 1966
	Simocephalus serrulatus		5.8				Sanders & Cope 1966
	Cypridopsis vidua		7.8				Sanders 1970
	Asellus brevicaudus		34.0				Sanders 1970
	Hyalella azteca	18.8	12.5	8.5		96 IC50-2.8	Wilson & Bond 1969
	Gammarus fasciatus	20	18	10			Sanders 1970
	Gammarus lacustris	16	15	11			Sanders 1969
	Palaemonetes kadiakensis		9.0				Sanders 1970
	Orconectes nais		22.0				Sanders 1970
	INSECTS						
	Callibaetis sp.	19.2	15.2	10.3			Wilson & Bond 1969
	Enallagma sp.	25.5	24.2	20.7			Wilson & Bond 1969
	Libellula sp.	>100	>100	>100			Wilson & Bond 1969
	Pteronarcys californica	42	8.4	7			Sanders & Cope 1968
	Limnephilus sp.	28.2	23.3	13.0			Wilson & Bond 1969
	Tendipedidae	15.7	12.5	7.8			Wilson & Bond 1969
DICLONE Fungicide (Phygon®)	FISH						
	Oncorhynchus sp.		0.048				Pimentel 1971
	Salmo gairdneri		0.048				Pimentel 1971
	Ictalurus sp.					24 hr LC50-0.14	Pimentel 1971
	Lepomis macrochirus	0.040	0.070				Johnson 1968
			0.120				Pimentel 1971
	CRUSTACEANS						
	Daphnia magna		0.025				Sanders 1970
	Cypridopsis vidua		0.120				Sanders 1970
	Asellus brevicaudus		0.200				Sanders 1970
	Gammarus fasciatus	0.30	0.24	0.10			Sanders 1970
	Gammarus lacustris	3.2	2.3	1.1			Sanders 1969
	Palaemonetes kadiakensis		0.45				Sanders 1970
	Orconectes nais		3.2				Sanders 1970
DICHLORVOS Insecticide	FISH						
	Salmo gairdneri	0.500					Cope 1963
	Lepomis macrochirus	1.0	0.70	0.48			Cope 1965b
				0.869			WQC 1972
	CRUSTACEANS						
	Daphnia pulex		0.000066				Sanders & Cope 1966
	Simocephalus serrulatus		0.00026				Sanders & Cope 1966
	Gammarus fasciatus			0.0004			Sanders 1972
	Gammarus lacustris	0.002	0.001	0.0005			Sanders 1969
	INSECTS						
	Pteronarcys californica	0.025	0.010	0.0001			Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DEILDRIN Insecticide	FISH						
	Oncorhynchus kisutch	0.0175	0.0153	0.0108		72 hr LC50-0.0144	Katz 1961
	Oncorhynchus tschawytscha	0.0079	0.0067	0.0061		72 hr LC50-0.0061	Katz 1961
	Salmo gairdneri	0.0157	0.0130	0.0099		72 hr LC50-0.0099	Katz 1961
		0.019	0.015	0.013			Cope 1965b
	Carassius auratus			0.037			Henderson et al. 1959
	Pimephales promelas			0.016			Henderson et al. 1959
	Poecilia latipinna					34 wks-chronic effects at 0.00075	Lane & Livingston, 1970
	Gasterosteus aculeatus	0.0207	0.0189	0.0153		72 hr LC50-0.0180	Katz 1961
	Lepomis gibbosus			0.0067		100 day EC-0.0017	Cairns & Scheir 1964
	Lepomis macrochirus	0.0055	0.0034	0.0028			Cope 1965b
	CRUSTACEANS						
	Daphnia carinata					64 hr EC50-0.250	Sanders & Cope 1966
	Daphnia magna	0.740				50 hr EC50-0.330	Sanders & Cope 1966
	Daphnia pulex		0.250				Sanders & Cope 1966
	Simocephalus serrulatus		0.190				Sanders & Cope 1966
	Asellus brevicaudus			0.005			Sanders 1972
	Gammarus fasciatus			0.600			Sanders 1972
	Gammarus lacustris	1.4	1.0	0.460			Sanders 1969
	Palaemonetes kadiakensis			0.020			Sanders 1972
	Orconectes nais			0.740			Sanders 1972
	INSECTS						
	Pteronarcella badia	0.0028	0.0015	0.0005			Sanders & Cope 1968
	Pteronarcys californica	0.006	0.0013	0.0005			Sanders & Cope 1968
				0.039		10 day LC50-0.021	Jensen & Gaufin 1966
	Acroneuria pacifica			0.024		10 day LC50-0.004	Jensen & Gaufin 1966
	Claassenia sabulosa	0.0045	0.0023	0.00058			Sanders & Cope 1968
DIOXATHION Insecticide Acaricide	FISH						
	Carassius auratus	42	42	32			Pickering et al. 1962
	Pimephales promelas	15	12	9.3			Pickering et al. 1962
	Poecilia reticulata	0.35	0.25	0.21			Pickering et al. 1962
	Lepomis cyanellus			0.061			Pickering et al. 1962
	Lepomis macrochirus	0.043	0.043	0.034			Pickering et al. 1962
	Micropterus salmoides			0.036			Pickering et al. 1962
	CRUSTACEANS						
	Gammarus fasciatus			0.0086			Sanders 1972
	Gammarus lacustris	0.83	0.69	0.27			Sanders 1969
DIPHENAMID Herbicide	FISH						
	Salmo gairdneri	150	110	97			Cope 1965b
	Lepomis macrochirus	92	80	75			Cope 1965b
	CRUSTACEANS						
	Daphnia magna		56				Sanders 1970
	Cypridopsis vidua		50				Sanders 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DIPHENAMID (contd)	Asellus brevicaudus		>100				Sanders 1970
	Gammarus fasciatus		>100				Sanders 1970
	Palaemonetes kadiakensis		58				Sanders 1970
	Orconectes nais		>100				Sanders 1970
DIQUAT Herbicide	FISH						
	Oncorhynchus tschawytscha	29.5	28.5				Gilderhus 1967
	Salmo gairdneri	90					Alabaster 1969
			11.2				Gilderhus 1967
	Esox lucius		16				Gilderhus 1967
	Carassius auratus		35				Gilderhus 1967
	Notropis atherinoides	180					Pimentel 1971
	Pimephales promelas	140, 260	26, 220	14, 130			Surber & Pickering 1962
	Lepomis macrochirus	91, 410	80, 210	72, 140			Surber & Pickering 1962
				35			Gilderhus 1967
	Micropterus salmoides	24	11	7.8			Surber & Pickering 1962
	Stizostedion vitreum			2.1			Gilderhus 1967
	CRUSTACEANS						
	Daphnia magna					8 days at 1ppm - toxic to adults	Wilson & Bond 1969
						8 days at 3ppm - toxic to all	Wilson & Bond 1969
	Hyalella azteca	0.580	0.120	0.048			Wilson & Bond 1969
	INSECTS						
	Callibaetis sp.	>100	37	16.4			Wilson & Bond 1969
	Enallagma sp,	>100	>100	>100			Wilson & Bond 1969
	Libellula sp.	>100	>100	>100			Wilson & Bond 1969
	Limnephilus sp.	>100	>65	>33			Wilson & Bond 1969
	Tendipedidae	>100	>100	>100			Wilson & Bond 1969
DISULFOTON Insecticide	FISH						
	Carassius auratus	7.5	7.2	7.2			Pickering et al. 1962
	Pimephales promelas			3.7, 4.1			Battelle 1971
	Poecilia reticulata	0.32	0.32	0.28			Pickering et al. 1962
	Lepomis macrochirus		0.040				Pimentel 1971
				0.064			Battelle 1971
	CRUSTACEANS						
	Gammarus fasciatus			0.021			Sanders 1972
	Gammarus lacustris	0.110	0.070	0.052			Sanders 1969
	Palaemonetes kadiakensis			0.038			Sanders 1972
	INSECTS						
	Pteronarcys californica	0.040	0.018	0.005			Sanders & Cope 1968
DIURON Herbicide	FISH						
	Salmo gairdneri		4.3				Cope 1965a
	Oncorhynchus kisutch		16, 42				Pimental 1971
	Lepomis macrochirus	12	7.4	4.0			Cope 1965b
	Micropterus salmoides		16.0				Sanborn et al. 1977

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
DIURON (contd)	CRUSTACEANS						
	Daphnia magna					26 IC50-47ppm	Crosby 1966
	Daphnia pulex		1.4				Sanders & Cope 1966
	Simocephalus serrulatus		2.0				Sanders & Cope 1966
	Gammarus fasciatus	2.5	1.8	0.700			Sanders 1970
	Gammarus lacustris	0.700	0.380	0.160			Sanders 1969
	INSECTS						
	Pteronarcys californica	3.6	2.8	1.2			Sanders & Cope 1968
ENDOSULFAN Insecticide (Thiodan®)	FISH						
	Salmo gairdneri	0.0021	0.0011	0.003		120 hr LC50-0.0003	Schoettger 1970
	Pimephales promelas				>0.0002<0.0004	Incipient LC50-0.00086	Macek et al. 1976
	Catostomus commersoni	0.0066 - 0.0081	0.0025 - 0.0028	0.0030 - 0.0035		120 hr LC50-0.0025, 0.0028	Schoettger 1970
	Poecilia reticulata	0.0046	0.0039	0.0037			Pickering & Henderson 1966
	Lepomis macrochirus	0.0036 - 0.0046	0.0033 - 0.0044	0.0033 0.0044			Schoettger 1970
	CRUSTACEANS						
	Daphnia magna	0.068-0.178	0.062-0.138	0.0529-0.0560		120 hr LC50-0.0475 - 0.0535	Schoettger 1970
					>0.0027<0.007		Macek et al. 1976
	Daphnia pulex		0.24				Pimentel 1971
	Gammarus lacustris	0.0092	0.0064	0.0058			Sanders 1969
	INSECTS						
	Ischnura sp.	0.235-0.275	0.120-0.175	0.0718-0.107		120 hr LC50-0.062 - 0.075	Schoettger 1970
	Pteronarcys californica	0.024	0.0056	0.0023			Sanders & Cope 1968
ENDOTHALL (Na, K) Herbicide	FISH						
	Oncorhynchus tschawytscha			136			WQC 1972
	Cyprinus carpio			175			Pimentel 1971
	Notropis lutrensis			105			Walker 1964
	Notropis umbratilus			95			Walker 1964
	Ictalurus melas			180			Walker 1964
	Ictalurus natalis			175			Walker 1964
	Lepomis macrochirus	390, 450	240, 320	160, 180			Surber & Pickering 1962
				125			Walker 1964
	Lepomis microlophus			125			Walker 1964
	Micropterus salmoides			120			Walker 1964
		560	320	200			Surber & Pickering 1962
	CRUSTACEANS						
	Daphnia magna					26 hr IC50-46	Pimentel 1971
	Gammarus fasciatus	2.0				24 hr LC50->100 (K salt)	Pimentel 1971
	Gammarus lacustris					96 hr no effect-100	Sanders 1969

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
ENDRIN Insecticide	FISH						
	Oncorhynchus kisutch	0.0013	0.0008	0.00051		72 hr LC50-0.00052	Katz 1961
	Oncorhynchus tschawytscha	0.0020	0.0012	0.0012			Katz 1961
	Salmo clarki			0.000113			Henderson
	Salmo gairdneri	0.00079	0.00058	0.00058			Katz 1961
		0.0018	0.0012	0.00086			Cope 1965b
	Carassius auratus			0.0019			Henderson et al. 1959
	Pimephalas promelas			0.0010			Henderson et al. 1959
	Ictalurus punctatus			0.0008			McCorkle et al. 1977
	Poecilia reticulata			0.0015			Henderson et al. 1959
	Gasterosteus aculeatus		0.00045	0.00044			Katz 1961
	Lepomis macrochirus	0.00035	0.00027	0.00025			Cope 1965b
		0.006	0.0016	0.0006			Henderson 1959
	CRUSTACEANS						
	Daphnia carinata					64 hr EC50-0.050	Sanders & Cope 1966
	Daphnia magna	0.900				50 hr EC50-0.352	Sanders & Cope 1966
	Daphnia pulex		0.020				Sanders & Cope 1966
	Simocephalus serrulatus		0.026				Sanders & Cope 1966
	Asellus brevicaudus			0.0015			Sanders 1972
	Gammarus fasciatus					120 LC50-0.0009	Sanders 1972
	Gammarus lacustris	0.0064	0.0047	0.003			Sanders 1969
	Palaemonetes kadiakensis					120 LC50-0.0004	Sanders 1972
	Orconectes nais			0.0032			Sanders 1972
	INSECTS						
	Pteronarcella badia	0.0028	0.0017	0.00054			Sanders & Cope 1968
	Pteronarcys californica	0.004	0.00096	0.00025			Sanders & Cope 1968
				0.0024		30 day LC50-0.0012	Jensen & Gaufin 1966
	Acroneuria pacifica			0.00032		30 day LC50-0.000035	Jensen & Gaufin 1966
	Claassenia sabulosa	0.0032	0.0084	0.00076			Sanders & Cope 1968
EPN Insecticide Acaricide	FISH						
	Pimephales promelas	0.32	0.29	0.25			Pickering 1962
				110			Solon & Nair 1970
	Lepomis macrochirus	0.18	0.13	0.10			Pickering 1962
	CRUSTACEANS						
	Gammarus fasciatus			0.007			Sanders 1972
	Gammarus lacustris	0.100	0.036	0.015			Sanders 1969
	Palaemonetes kadiakensis			0.00056			Sanders 1972
EPTC Herbicide	FISH						
	Pimephales promelas			27			Herbicide Handbook 1970
	Gambusia affinis			17			Sanborn et al. 1977
	Salmo gairdneri			19, 21			Herbicide Handbook 1970
	CRUSTACEANS						
	Daphnia magna		9.4	4.7			Sanborn et al. 1977
	Gammarus fasciatus	43	35	23			Sanders 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
ETHION Insecticide Acaricide (Nialate®)	FISH						
	Salmo gairdneri			0.56			WQC 1972
	Salmo clarki			0.72			WQC 1972
	Pimephales promelas		2.5	2.4		Soft water	Pickering & Henderson 1966
	Ictalurus punctatus			7.5			WQC 1972
	Poecilia reticulata			0.13			Pickering & Henderson 1966
	Lepomis macrochirus	0.21	0.14	0.13			Pickering & Henderson 1966
			0.23	0.22			Pimentel 1971
	CRUSTACEANS						
	Daphnia magna		0.00001				Pimentel 1971
	Gammarus fasciatus			0.0094			Sanders 1972
	Gammarus lacustris	0.0056	0.0032	0.0018			Sanders 1969
	Palaemonetes kadiakensis			0.0057			Sanders 1972
	INSECTS						
	Pteronarcys californica	0.024	0.014	0.0028			Sanders & Cope 1968
FENAC Herbicide	FISH						
	Salmo gairdneri		7.5				Cope 1965a
	Lepomis macrochirus	61	50	41			Cope 1965b
	CRUSTACEANS						
	Daphnia magna		>100				Sanders 1970
	Daphnia pulex		4.5				Sanders & Cope 1966
	Simocephalus serrulatus		6.6				Sanders & Cope 1966
	Cypridopsis vidua		>100				Sanders 1970
	Asellus brevicaudus		>100				Sanders 1970
	Gammarus fasciatus		>100				Sanders 1970
	Gammarus lacustris	22	18	12			Sanders 1969
	Palaemonetes kadiakensis		>100				Sanders 1970
	INSECTS						
	Pteronarcys californica	170	70	60			Sanders & Cope 1968
FENTHION Insecticide (Baytex®)	FISH						
	Oncorhynchus kisutch			1.32			Macek & McAllister 1970
	Salmo gairdneri			0.93			Macek & McAllister 1970
		0.84	0.80	0.76			Cope 1965b
	Salmo trutta			1.33			Macek & McAllister 1970
	Pimephales promelas	3.3-3.5	3.2-3.5	3.2-3.5			Pickering & Henderson 1966
				2.44			Macek & McAllister 1970
	Ictalurus melas			1.62			Macek & McAllister 1970
	Ictalurus punctatus			1.68			Macek & McAllister 1970
	Poecilia reticulata	5.0	3.6	3.1			Pickering & Henderson 1966
	Lepomis macrochirus	3.7	3.7	3.1			Pickering & Henderson 1966
				1.38			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
FENTHION (contd)	Lepomis microlophus			1.88			Macek & McAllister 1970
	Micropterus salmoides			1.54			Macek & McAllister 1970
	Perca flavescens			1.65			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia pulex		0.0008				Sanders & Cope 1966
	Simocephalus serrulatus		0.00092				Sanders & Cope 1966
	Asellus brevicaudus			1.80			Sanders 1972
	Gammarus fasciatus			0.110			Sanders 1972
	Gammarus lacustris	0.015	0.011	0.0084			Sanders 1969
	Palaemonetes kadiakensis			0.050			Sanders 1972
	Orconectes nais						Sanders 1972
	INSECTS						
	Pteronarcys californica	0.130	0.039	0.0045			Sanders & Cope 1968
	Acroneuria pacifica			0.0051		30 day LC50-0.00064	Jensen & Gaufin 1966
HEPTACHLOR Insecticide	FISH						
	Oncorhynchus kisutch	0.0619	0.0604	0.0590		72 hr LC50-0.0604	Katz 1961
	Oncorhynchus tschawytscha	0.0324	0.0266	0.0173		72 hr LC50-0.023	Katz 1961
	Salmo gairdneri	0.015	0.009	0.008			Cope 1965b
		0.0367	0.0338	0.0194		72 hr LC50-0.0259	Katz 1961
	Carassius auratus			0.230			Henderson et al. 1959
	Pimephales promelas			0.056,.094			Henderson et al. 1959
	Poecilia reticulata			0.107			Henderson et al. 1959
	Gasterosteus aculeatus	0.121	0.112	0.112			Katz 1961
	Lepomis macrochirus		0.023	0.017		6 hr LC50-0.062	Cope 1963
	CRUSTACEANS						
	Daphnia carinata					64 hr EC50-0.020	Sanders & Cope 1966
	Daphnia magna					50 hr EC50-0.0578	Sanders & Cope 1966
			0.078		>0.0125<0.025		Macek et al. 1976
	Daphnia pulex		0.042				Sanders & Cope 1966
	Simocephalus serrulatus		0.047				Sanders & Cope 1966
	Gammarus fasciatus		0.040				Sanders 1972
	Gammarus lacustris	0.150	0.100	0.029			Sanders 1969
	Palaemonetes kadiakensis			0.0018			Sanders 1972
	Orconectes nais			0.0078			Sanders 1972
	INSECTS						
	Pteronarcella badia	0.006	0.004	0.0009			Sanders & Cope 1968
	Pteronarcys californica	0.008	0.0056	0.0011			Sanders & Cope 1968
	Claassenia sabulosa	0.009	0.0064	0.0028			Sanders & Cope 1968
LINDANE Insecticide	FISH						
	Oncorhychus kisutch			0.041			Macek & McAllister 1970
	Salmo gairdneri			0.027			Macek & McAllister 1970
		0.030	0.022	0.022			Cope 1965b
		0.042	0.041	0.038		72 hr LC50-0.039	Katz 1961
	Salmo trutta			0.002			Macek & McAllister 1970
	Salvelinus fontinalis				>0.0088<0.0166	ILC50-0.026	Macek et al. May 1976
	Carassius auratus			0.131			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
LINDANE (contd)	Cyprinus carpio			0.090			Macek & McAllister 1970
	Pimephales promelas			0.087	>0.0091<0.0235	ILC50-0.069	Macek et al. May 1976
	Ictalurus melas			0.064			Macek & McAllister 1970
	Ictalurus punctatus			0.044			Macek & McAllister 1970
	Lepomis macrochirus			0.068			Macek & McAllister 1970
					>0.0091<0.0125	ILC50-0.030	Macek et al. May 1976
	Lepomis microlophus		0.053	0.083			Cope 1965a Macek & McAllister 1970
	Micropterus salmoides			0.032			Macek & McAllister 1970
	Perca flavescens			0.068			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia magna	1.10					
	Daphnia pulex		0.485		>0.011<0.019		Sanders & Cope 1966 Macek et al. 1976
	Simocephalus serrulatus		0.460				Sanders & Cope 1966
	Asellus brevicaudus		0.520,0.880				Sanders & Cope 1966
	Gammarus fasciatus		0.039	0.010	>0.0043<0.0086		Sanders 1972 Macek et al. 1970
	Gammarus lacustris	0.120	0.088	0.010 0.048			Sanders 1972 Sanders 1969
	INSECTS						
	Pteronarcys californica	0.012	0.008	0.0045			Sanders & Cope 1968
	Chironomus tentans		0.207		>0.0022<0.005		Macek et al. 1976
MALATHION Insecticide Acaricide	FISH						
	Oncorhynchus kisutch			0.101			
	Onçorhynchus tschawytscha			0.120			Macek & McAllister 1970
	Salmo gairdneri	0.0245 0.085-.130	0.0239	0.023 0.079-0.120	0.068-0.110	72 hr LC50-0.0236	Macek & McAllister 1970 Katz 1961
	Salvelinus fontinalis	0.120			0.170		Cope 1965b
	Carassius auratus			0.090-0.200			Macek & McAllister 1970
	Cyprinus carpio			10.7			Macek & McAllister 1970
	Notropis lutrensis			6.59			Macek & McAllister 1970
	Pimephales promelas	0.040	0.036	0.025			Macek & McAllister 1970
				12.5			Henderson & Pickering 1958
	Ictalurus melas			10.45	>0.20<0.58		Mount & Stephan 1967
	Ictalurus punctatus			12.9			Macek & McAllister 1970
	Poecilia reticulata	0.93	0.88	8.97			Macek & McAllister 1970
	Gasterosteus aculeatus	0.0969	0.0940	0.84			Pickering 1970
	Leopomis cyanellus			0.0940			Katz 1961
	Leopomis macrochirus			0.120			Macek & McAllister 1970
	Lepomis microlophus			0.110	>0.0036<0.0074		Eaton 1970
	Micropterus salmoides			0.170			Macek & McAllister 1970
	Perca flavescens			0.285			Macek & McAllister 1970
				0.263			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
MALATHION (contd)	CRUSTACEANS						
	Daphnia magna	0.0009				50 hr EC50-0.009	Sanders & Cope 1966
	Daphnia pulex		0.0018				Sanders & Cope 1966
	Simocephalus serrulatus		0.0035				Sanders & Cope 1966
	Asellus brevicaudus			3.0			Sanders 1972
	Gammarus fasciatus			0.00076			Sanders 1972
	Gammarus lacustris	0.0038	0.0018	0.0010			Sanders 1969
	Gammarus pseudolimneaus					30 day LC50-0.000023	WQC 1972
	Palaemonetes kadiakensis			0.012			Sanders 1970
	Orconectes nais			0.180			Sanders 1970
	INSECTS						
	Ophiogomphus rupinsulensis					30 day LC50-0.0052	WQC 1972
	Pteronarcella badia	0.010	0.006	0.0011			Sanders & Cope 1968
	Pteronarcys californica	0.035	0.020	0.010			Sanders & Cope 1968
	Pteronarcys dorsata					30 day LC50-0.0111	WQC 1972
	Acroneuria lycorias			0.001		30 day LC50-0.0003	WQC 1972
	Claassenia sabulosa	0.013	0.006	0.0028-0.0056			Sanders & Cope 1963
	Hydropsyche bettoni					30 day LC50-0.00034	WQC 1972
MCPA Herbicide	FISH						
	Lepomis macrochirus		1.5				Hughes & Davis 1964
	CRUSTACEAN						
	Daphnia magna					EC50>100	Pimentel 1971
METHOXYCHLOR Insecticide	FISH						
	Oncorhynchus kisutch	0.0662	0.0662	0.0662			Katz 1961
	Oncorhynchus tschawytscha	0.0280	0.0279	0.0279			Katz 1961
	Salmo gairdneri	0.052	0.0072				Sanborn et al. 1977
				0.0626			Katz 1961
	Carassius auratus			0.056			Henderson et al. 1959
	Pimephales promelas			0.0075		Application Factor-0.017	Effects of Pesticides in water 1972
				0.064			Henderson et al. 1959
	Poecilia reticulata			0.120			Henderson et al. 1959
	Gasterosteus aculeatus	0.0936	0.0864	0.0864			Katz 1961
	Lepomis macrochirus	0.031		0.062			Henderson et al. 1959
	Perca flavescens			0.020			Merna (WQC 1972)
	CRUSTACEANS						
	Daphnia magna	0.0037				50 EC50-0.0036	Sanders & Cope 1966
	Daphnia pulex		0.00078				Sanders & Cope 1966
	Simocephalus serrulatus		0.005				Sanders & Cope 1966
	Asellus brevicaudus			0.0032			Sanders 1972
	Gammarus fasciatus			0.0019			Sanders 1972
	Gammarus lacustris	0.0029	0.0013	0.0008			Sanders 1969
	Gammarus pseudolimneaus			0.00061		TL50 chronic-0.0003	QCW 1976
	Palaemonetes kadiakensis			0.001			Sanders 1972
	Ornectes nais			0.0005			Sanders 1972

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
METHOXYCHLOR (contd)	INSECTS						
	Pteronarcys californica	0.030	0.008	0.0014			Cope 1965b
	Taeniopteryx nivalis			0.00098			Merna (WQC 1972)
METHYL PARATHION Insecticide	FISH						
	Oncorhynchus kisutch			5.3			Macek & McAllister 1970
	Salmo gairdneri			2.75			Macek & McAllister 1970
	Salmo trutta			4.74			Macek & McAllister 1970
	Carassius auratus	14	12	12			Pickering et al. 1962
				9			Macek & McAllister 1970
	Cyprinus carpio			7.13			Macek & McAllister 1970
	Pimephales promelas			8.9			Macek & McAllister 1970
	Ictalurus melas			6.64			Macek & McAllister 1970
	Ictalurus punctatus			5.71			Macek & McAllister 1970
	Poecilia reticulata	11	9.8	9.8			Pickering et al. 1962
	Lepomis macrochirus	9.8	8.6	2.4			Pickering et al. 1962
				5.72			Macek & McAllister 1970
	Lepomis microlophus			5.17			Macek & McAllister 1970
	Micropterus salmoides			5.22			Macek & McAllister 1970
	Perca flavescens			3.06			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia magna		0.0048				Pimentel 1971
MEVINPHOS Insecticide Acaricide	FISH						
	Salmo gairdneri	0.034	0.017	0.012			Cope 1965b
	Lepomis macrochrus	0.041	0.037	0.023			Cope 1965b
	Micropterus salmoides			0.110			WQC 1972
	CRUSTACEANS						
	Daphnia pulex		0.00016				Sanders & Cope 1966
	Simocephalus serrulatus		0.00043				Sanders & Cope 1966
	Gammarus fasciatus			0.0028			Sanders 1972
	Gammarus lacustris	0.650	0.310	0.130			Sanders 1969
	Palaemonetes kadiakensis			0.012			Sanders 1972
	INSECTS						
	Pteronarcys californica	0.056	0.009	0.005			Sanders & Cope 1968
MEXACARBATE Insecticide Acaricide (Zectran®)	FISH						
	Oncorhynchus kisutch	12.9-32.0		4.0-23.0			Macek et al. 1977
	Salmo gairdneri		8.0				Pimentel 1971
				10.2			Mack & McAllister 1970
	Salmo trutta	26		20			Macek et al. 1977
	Carassius auratus			19.14			Mack & McAllister 1970
	Cyprinus carpio			13.4			Macek & McAllister 1970
	Pimephales promelas	23.7		23.7			Macek et al. 1977
	Ictaluras melas			16.7			Macek & McAllister 1970
	Ictaluras punctatus			11.4			Macek & McAllister 1970
	Lepomis macrochirus	>2.5-27.8		0.6-22.9			Macek et al. 1977

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
MEXACARBATE (contd)	Lepomis microlophus			16.7			Macek & McAllister 1970
	Micropterus salmoides			14.7			Macek & McAllister 1970
	Perca flavescens	17.1		16.2			Macek et al. 1977
				2.48			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia pulex		0.010				Sanders & Cope 1966
	Simocephalus serrulatus		0.013				Sanders & Cope 1966
	Gammarus fasciatus			0.040			Sanders 1972
	Gammarus lacustris	0.086	0.076	0.046			Sanders 1969
	Palaemonetes kadiakensis			0.083		20 day LC50-0.025	Sanders 1972
	INSECTS						
	Pteronarcys californica	0.032	0.016	0.010			Sanders & Cope 1968
MONURON Herbicide	FISH						
	Oncorhynchus kisutch	115	110				Bond et al. 1960
	Ictalurus punctatus	75					Sanborn et al. 1977
	Mugil cephalus		16.3				Pimentel 1971
NALED Insecticide	FISH						
	Salmo gairdneri	0.24-1.3					Pimentel 1971
				0.132			WQC 1972
	Salmo trutta		0.078				Pimentel 1971
	Lepomis macrochirus	0.220	0.220	0.180			Cope 1965b
	CRUSTACEANS						
	Daphnia pulex		0.00035				Sanders & Cope 1966
	Simocephalus serrulatus		0.0011				Sanders & Cope 1966
	Asellus brevicaudus			0.230			Sanders 1972
	Gammarus fasciatus			0.014			Sanders 1972
	Gammarus lacustris	0.240	0.160	0.110			Sanders 1969
	Palaemonetes kadiakensis			0.090			Sanders 1972
	Orconectes nais			1.80			Sanders 1972
	INSECTS						
	Pteronarcys californica	0.027	0.016	0.008			Sanders & Cope 1968
PARAQUAT Herbicide	FISH						
	Lepomis macrochirus	400	100				Sanborn et al. 1977
	CRUSTACEANS						
	Daphnia magna					26 hr IC50-11.0	Crosby 1966
	Daphnia pulex		3.7				Sanders & Cope 1966
	Simocephalus serrulatus		4.0				Sanders & Cope 1966
	Gammarus lacustris	38	18	11			Sanders 1969
	INSECTS						
	Pteronarcys californica			>100			Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
PARATHION	FISH						
Insecticide	Salmo gairdneri		2				Sanders 1969
	Salvelinus fontinalis			1.76			Spacie 1975
	Pimephales promelas	2.1-3.0	1.8-3.0	1.3-3.0			Pickering et al. 1962
	Ictalurus nebulosus			1.41			Spacie 1975
	Gambusia affinis		0.61-0.95			30 days at 0.030-tremors	WQC 1976
	Poecilia reticulata			0.056			
	Lepomis macrochirus	0.10-0.26	0.10-0.26	0.095-0.26			Pickering et al. 1962
				0.5			Spacie 1975
	Morone saxatilis			0.018			Korn & Earnest 1974
	Lepomis cyanellus			0.42			Pickering et al. 1962
	Micropterus salmoides			0.19			Pickering
	CRUSTACEANS						
	Daphnia magna	0.0008		0.00062		50 hr EC50-0.0008	Sanders & Cope 1966
						21 day LC50-0.00014	Spacie 1975
	Daphnia pulex		0.0006				Sanders & Cope 1966
	Simocephalus serrulatus		0.00037				Sanders & Cope 1966
	Asellus brevicaudus			0.600			Sanders 1972
	Gammarus fasciatus			0.0004		43 day LC50-0.00007	Spacie 1975
	Gammarus lacustris	0.012	0.006	0.0035			Sanders 1969
	Palaemonetes kadiakensis			0.0015			Sanders 1972
	Ornectes nais			0.00004			Sanders 1972
	INSECTS						
	Ephemerella subvaria			0.00016		30 day LC50-0.000056	WQC 1972
	Ophiogomphus rupinsulensis			0.00325		30 day LC50-0.00022	WQC 1972
	Pteronarcys californica	0.028	0.011	0.0054			Sanders & Cope 1968
				0.036		30 day LC50-0.0022	Jensen & Gaufin 1964
	Pteronarcys dorsata			0.003		30 day LC50-0.0090	WQC 1972
	Pternarcella badia	0.008	0.0056	0.0042			Sanders & Cope 1968
	Acroneuria lycorias					30 day LC50-0.000013	WQC 1972
	Arconeuria pacifica					5 day LC50-0.00093	Jensen & Gaufin 1964
	Claassenia sabulosa	0.0088	0.0035	0.0015			Sanders & Cope 1968
	Hydropsyche bettoni					30 day LC50-0.00045	WQC 1972
	Hydropsyche californica			0.00043			Gaufin et al. 1965
	Chironomus tentans			0.031			Spacie 1975
PHOSPHAMIDON	FISH						
Insecticide	Salmo gairdneri					18 hr LC50-5.0	Cope 1963
	Pimephales promelas			100			WQC 1972
	Ictalurus punctatus			70			WQC 1972
	Lepomis macrochirus			4.5			WQC 1972
	CRUSTACEANS						
	Daphnia pulex	0.0088					Sanders & Cope 1966
	Simocephalus serrulatus	0.0066,.012					Sanders & Cope 1966
	Gammarus fasciatus			0.016			Sanders - WQC 1972
	Gammarus lacustris	0.0084	0.0038	0.0028			Sanders 1969
	Orconectes nais			7.5			Sanders - WQC 1972

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
PHOSPHAMIDON (contd)	INSECTS						
	Pteronarcys californica	1.400	0.460	0.150			Sanders & Cope 1968
PICLORAM Herbicide	FISH						
	Carassius auratus	<36				acid	Sanborn et al. 1977
	Ictalurus punctatus	2.2				isooctyl ester	Sanborn et al. 1977
	Rasbora heteromorpha	66	44				Alabaster 1969
	CRUSTACEANS						
	Gammarus lacustris	50	48	27			Sanders 1970
	INSECTS						
	Pteronarcys californica	120	90	48			Sanders & Cope 1968
PROPACHLOR Herbicide	FISH						
	Pimephales promelas			0.49			Herbicide Handbook 1970
	Lepomis macrochirus (fingerling)			1.30			Herbicide Handbook 1970
PROPHAM Plant growth regulator	CRUSTACEANS						
	Daphnia pulex		10				Sanders & Cope 1966
	Gammarus fasciatus	54	22	19			Sanders 1970
	Gammarus lacustris	20	16	10			Sanders 1969
	Simocephalus serrulatus		10				Sanders & Cope 1968
PYRETHRUM/ PYRETHRINS Insecticide	FISH						
	Salmo gairdneri			0.023			Mauck et al. 1976
	Ictalurus punctatus			0.132			Mauck et al. 1976
	Oncorhynchus kisutch			0.023			Mauck et al. 1976
	Perca flavescens			0.045			Mauck et al. 1976
	CRUSTACEANS						
	Daphnia pulex		0.025				Sanders & Cope 1966
	Simocephalus serrulatus		0.042				Sanders & Cope 1966
	Gammarus lacustris	0.028	0.018	0.012			Sanders 1969
	INSECTS						
	Pteronarcys californica	0.010	0.0064	0.001			Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
ROTENONE Insecticide Acaricide	FISH						
	Oncorhynchus kisutch (embryos)	0.150					Pimentel 1971
	Salmo gairdneri	0.032*		0.057**			*Wilber 1969 **Kemp et al. 1973
	Carassius auratus						
	Pimephalus promelas						
	Ictalurus punctatus						
	Poecilia reticulata						
	Lepomis macrochirus	0.024*		0.023**			*Wilber 1969 **Pimental 1971
	CRUSTACEANS						
	Daphnia pulex		0.100				Sanders & Cope 1966
	Simocephales serrulatus		0.190				Sanders & Cope 1966
	Gammarus lacustris	6.0	3.5	2.6			Sanders 1969
	INSECTS						
	Pteronarcys californica	2.9	1.1	0.380			Sanders & Cope 1968
SILVEX Herbicide	FISH						
	Oncorhynchus tschawytscha						
	Salmo gairdneri		1.4			PGBE	Cope 1965a
	Notropis species						
	Pimephales promelas	8.9-75	7.2-75	7.2-75			Surber & Pickering 1962
	Leopomis macrochirus		16.6,70.0			PGBE,BEE	Sanders 1970
	CRUSTACEANS						
	Daphnia magna		0.18,2.1			BEE,PGBE	Sanders 1970
	Cypridopsis vidua		0.200,4.9			BEE,PGBE	Sanders 1970
	Asellus brevicaudus		0.500,40			BEE,PGBE	Sanders 1970
	Gammarus fasciatus	1.2,1.8	0.78,1.0	.25,0.840		BEE,PGBE	Sanders 1970
	Palaemonetes kadiakensis		3.2, 8.0			BEE,PGBE	Sanders 1970
	Orconectes nais		60,>100			48 hr LC50>100 (PGBE)	Sanders 1970
	Daphnia pulex		2.0 (EC)			BEE,PGBE	Sanders & Cope 1966
	Simocephalus serrulatus		2.4 (EC)				Sanders & Cope 1966
	INSECTS						
	Pteronarcys californica	5.2	0.76	0.34			Sanders & Cope 1966
SIMAZINE Herbicide	FISH						
	Oncorhynchus kisutch		6.6				Bond et al. 1960
	Oncorhynchus tschawytscha	7.0					
	Salmo gairdneri	68	60	56			Cope 1965b
	Pimephales promelas					72 hr LC50-0.50	
	Lepomis macrochirus	130	118	118			Cope 1965b
	Rasbora heteromorpha	95	85				Alabaster 1969

TABLE B.1. (contd)

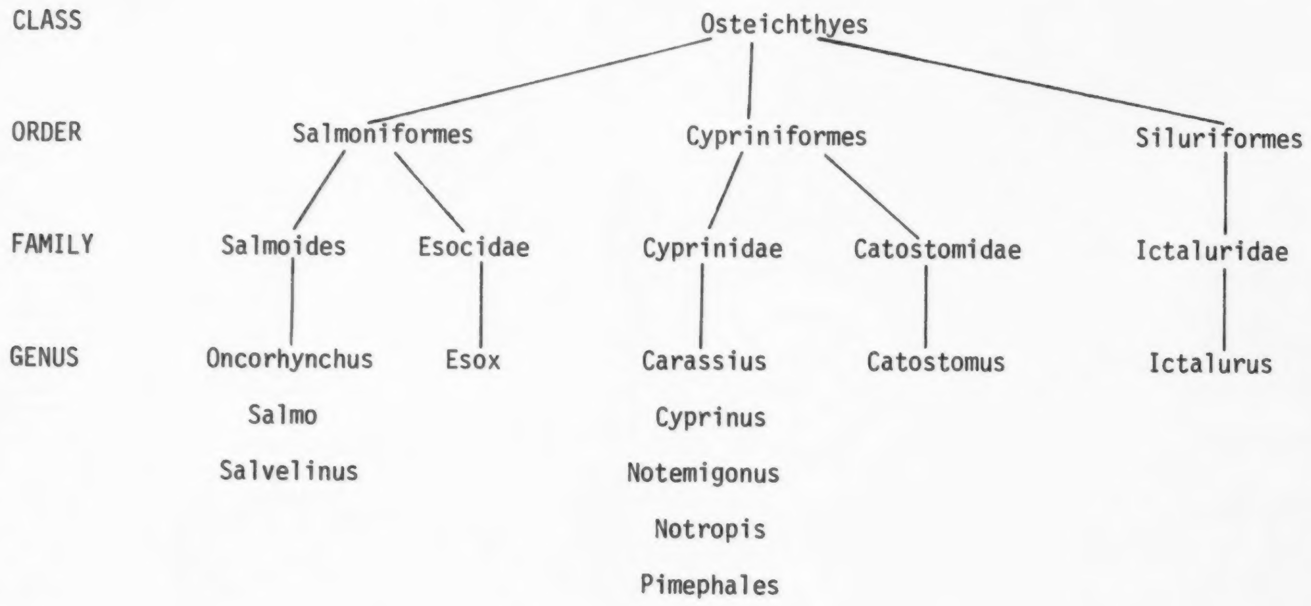
Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
SIMAZINE (contd)	CRUSTACEANS						
	Daphnia magna		1.0				Sanders 1970
	Cypridopsis vidua		3.2				Sanders 1970
	Asellus brevicaudus		>100				Sanders 1970
	Gammarus fasciatus		>100				Sanders 1970
	Gammarus lacustris	30	21	13			Sanders 1969
	Palaemonetes kadiakensis		>100				Sanders 1970
	Orconectes nais		>100				Sanders 1970
2,4,5-T Herbicide	FISH						
	Lepomis macrochirus	2.0	2.0			BEE acid	Kenaga 1974
		26	26			PGBE acid	Kenaga 1974
	Rasbora heteromorpha	1	1			Butyl ester	Alabaster 1969
	CRUSTACEANS						
	Daphnia pulex		3.2				Sanders & Cope 1966
	Simocephalus serrulatus		4.9				Sanders & Cope 1966
	Cypridopsis vidua	0.07-0.65	<0.65				Kenaga 1974
	Asellus brevicaudus	>0.72		>0.72		BEE acid	Kenaga 1974
		0.65-6.5		0.07-6.5		PGBE acid	Kenaga 1974
	Gammarus fasciatus	0.07-0.72		0.07-0.72		BEE acid	Kenaga 1974
	Palaemonetes kadiakensis	>7.2		0.72-7.2		BEE acid	Kenaga 1974
		0.65-6.5		0.07-0.6.5		PGBE acid	Kenaga 1974
TEMEPHOS Larvicide (Abate®, Biothion®)	FISH						
	Salmo gairdneri			0.158			WQC 1972
	CRUSTACEAN						
	Gammarus lacustris	0.960	0.640	0.082			Sanders 1969
	INSECT						
	Pteronarcys californica	0.120	0.100	0.010			Sanders & Cope 1968
TEPP Aphicide Acaricide	FISH						
	Carassius auratus	21	21	21			Pickering et al. 1962
	Pimephales promelas	2.1	2.1	2.1			Pickering et al. 1962
	Poecilia reticulata	1.8	1.8	1.8			Pickering et al. 1962
	Lepomis macrochirus	1.3	1.3	1.3			Pickering et al. 1962
	CRUSTACEANS						
	Gammarus fasciatus			0.210			Sanders 1972
	Gammarus lacustris	0.074	0.052	0.039			Sanders 1969
TOXAPHENE Insecticide	FISH						
	Oncorhynchus kisutch	0.0130	0.0105	0.0094		72 hr LC50-0.010	Katz 1961
				0.008			Macek & McAllister 1970
	Oncorhynchus tschawytscha	0.0079	0.0033	0.0025		72 hr LC50-0.0027	Katz 1961
	Salmo gairdneri	0.0115	0.0084	0.0084			Katz 1961
				0.011			Macek & McAllister 1970

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
TOXAPHENE (contd)	Salmo trutta			0.003			Macek & McAllister 1970
	Salvelinus fontinalis			0.0108		90 days at 0.000039 no effect	Mayer et al. 1975
	Carassius auratus			0.014			Macek & McAllister 1970
	Cyprinus carpio			0.004			Macek & McAllister 1970
	Pimephales promelas			0.014			Macek & McAllister 1970
					>0.000025<0.000054		Mayer et al. 1977
	Ictalurus melas			0.005			Macek & McAllister 1970
	Ictalurus punctatus			0.013			Macek & McAllister 1970
					>0.000049<0.000072		Mayer et al. 1977
	Poecilia reticulata			0.020			Henderson et al. 1959
	Gasterosteus aculeatus		0.012	0.0086		72 hr LC50-0.0098	Katz 1961
	Lepomis macrochirus			0.0035			Henderson et al. 1959
	Lepomis microlophus			0.013			Macek & McAllister 1970
	Micropterus salmoides			0.002			Macek & McAllister 1970
	Perca flavescens			0.012			Macek & McAllister 1970
	CRUSTACEANS						
	Daphnia pulex		0.015				Sanders & Cope 1966
	Simocephalus serrulatus		0.019				Sanders & Cope 1966
	Gammarus fasciatus			0.006			Sanders 1972
	Gammarus lacustris	0.180	0.070	0.026			Sanders 1969
	Palaemonetes kadiakensis			0.028			Sanders 1972
	INSECTS						
	Pteronarcella badia	0.0092	0.0056	0.0030			Sanders & Cope 1968
	Pteronarcys californica	0.018	0.007	0.0023			Sanders & Cope 1968
	Claassenia sabulosa	0.006	0.0032	0.0013			Sanders & Cope 1968
TRICHLORFON Insecticide (Dipterex®)	FISH						
	Salmo gairdneri	28	3.2	1.4			Cope 1965b
	Carassius auratus	>1000	320	100			Pickering et al. 1962
	Pimephalas promelas			110			Pickering et al. 1962
	Lepomis macrochirus	12	7.2	3.8			Pickering et al. 1962
		5.6	1.6	0.26			Cope 1965b
	Poecilia reticulata	120	23	7.2			Pickering et al. 1962
	CRUSTACEANS						
	Daphnia carinata					64 hr EC50-0.00025	Sanders & Cope 1965
	Daphnia magna	0.00012					Sanders & Cope 1965
	Daphnia pulex		0.00018				Sanders & Cope 1966
	Simocephalus serrulatus		0.00032-0.00070				Sanders & Cope 1966
	Gammarus lacustris	0.092	0.060	0.0040			Sanders 1969
	INSECTS						
	Pteronarcella badia	0.050	0.022	0.011			Sanders & Cope 1968
	Pteronarcys californica	0.320	0.180	0.035			Sanders & Cope 1968
	Acroneuria pacifica			0.0165			Jensen & Gaufin 1964
	Claassenia sabulosa	0.110	0.070	0.022			Sanders & Cope 1968

TABLE B.1. (contd)

Pesticide	Organism	24 hr LC50	48 hr LC50	96 hr LC50	MATC	Additional Effects	Reference
TRIFLURALIN Herbicide	FISH						
	Salmo gairdneri	0.014, 0.210	0.011, 0.130	0.010, 0.086			Cope 1965b
	Pimephales promelas				>1.9<5.1	IC50-0.115	Macek et al. 1976
	Ictalurus punctatus			0.417			McCorkle et al. 1977
	Lepomis macrochirus	0.023, 0.100	0.020, 0.096	0.018, 0.068			Cope 1965b
	CRUSTACEANS						
	Daphnia magna		0.193		>2.4<7.2		Macek et al. 1976
			0.56				Sanders & Cope 1966
	Daphnia pulex		0.240				Sanders & Cope 1966
	Simocephalus serrulatus		0.450				Sanders 1970
	Cypridopsis vidua		0.25				Sanders 1970
	Asellus brevicaudus		2.0				Sanders 1970
	Gammarus fasciatus	3.2	1.8	1.0			Sanders 1970
	Gammarus lacustris	8.8	5.6	2.2			Sanders 1969
	Palaemonetes kadiakensis		1.2				Sanders 1970
	Orconectes nais		50.0				Sanders 1970
	INSECTS						
	Pteronarcys californica	13	4.2	3.0			Sanders & Cope 1968
VERNOLATE Herbicide	FISH						
	Salmo gairdneri (fingerling)			9.6,10.8			Herbicide Handbook 1970
	Gambusia affinis			14.5			Herbicide Handbook 1970
	Lepomis macrochirus	9.7	9.2	4.0			Cope 1975b
	CRUSTACEANS						
	Daphnia magna		1.10				Sanders 1970
	Cpridopsis vidua		0.24				Sanders 1970
	Asellus brevicaudus		5.60				Sanders 1970
	Gammarus fasciatus	24.0	18.0	13.0			Sanders 1970
	Gammarus lacustris	8.4	5.0	1.8			Sanders 1969
	Palaemonetes kadiakensis		1.9				Sanders 1970
	Orconectes nais		24.0				Sanders 1970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GENUS
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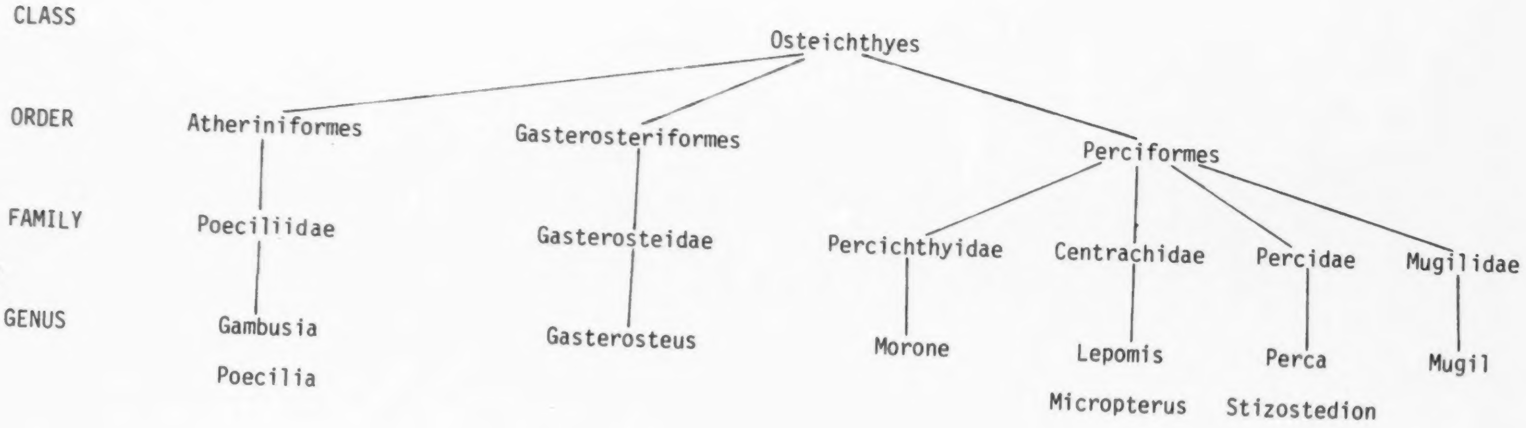
Salmoniformes
Cypriniformes
Siluriformes
Salmoides
Esocidae
Cyprinidae
Catostomidae
Ictaluridae
Oncorhynchus
Salmo
Salvelinus
Esox
Carassius
Cyprinus
Notemigonus
Notropis
Pimephales
Catostomus
Ictalurus

Figure B.1. A phylogenetic chart of fish used in this report.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GENUS
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Gasterosteriformes
Perciformes
Poeciliidae
Gasterosteidae
Percichthyidae
Centrachidae
Percidae
Mugilidae
Gambusia
Poecilia
Gasterosteus
Morone
Lepomis
Micropterus
Perca
Stizostedion
Mugil

Figure B.1. (contd)

TABLE B.2. SCIENTIFIC AND COMMON NAMES OF FISH USED IN THIS REPORT.

Scientific Name	Common Name
Oncorhynchus kisutch	coho salmon
Oncorhynchus tschawytscha	chinook
Salmo clarki	cutthroat trout
Salmo gairdneri	rainbow trout
Salmo trutta	brown trout
Salvelinus fontinalis	brook trout
Salvelinus namaycush	lake trout
Esox lucius	northern pike
Carassius auratus	goldfish
Cyprinus carpio	carp
Notemigonus crysoleucas	golden shiner
Notropis atherinoides	emerald shiner
Notropis lutrensis	red shiner
Notropis umbratilus	redfin shiner
Pimephales notatus	bluntnose minnow
Pimephales promelas	fathead minnow
Rasbora heteromorpha	harlequin
Catostomus commersoni	white sucker
Ictalurus melas	black bullhead
Ictalurus natalis	yellow bullhead
Ictalurus nebulosus	brown bullhead
Ictalurus punctatus	channel catfish
Gambusia affinis	mosquito fish
Poecilia latipinna	sailfin molly
Poecilia reticulata	guppy
Gasterosteus aculeatus	threespine stickleback
Lepomis cyanellus	green sunfish
Lepomis gibbosus	pumpkinseed fish
Lepomis macrochirus	bluefill sunfish
Lepomis microlophus	redear sunfish
Micropterus dolomieui	smallmouth bass
Micropterus salmoides	largemouth bass
Perca flavescens	yellow perch
Stizostedion vitreum	walleye
Mugil cephalus	striped mullet
Morone saxatilis	striped bass

TABLE B.3. PESTICIDE CLASSES

	Solubility (mg/1)	Kd	Soil Persistence	Water Persistence
ORGANOCHLORINES				
CHLORINATED HYDROCARBONS				
Aldrin	.011-.2	7×10^4	T/2 1-4 yr	40% - 4 wks 20% - 8 wks
Chlordane	Very low	5×10^4	T/2 2-4 yr	85% - 8 wks
DDT	.01-.037	1×10^5	T/2 3-10 yr	100% - 4 wks
Heptachlor	.056	1×10^4	T/2 7-10 yr	25% - 2 wks
Isodrin		7×10^4	T/2 4-8 yr	
Lindane	10	1×10^3	1 yr	
Mirex	.001	5×10^4	very stable	
TDE (DDD)	ins	5×10^4		
Toxaphene	1.5	5×10^4	4-16 yr	9-10 yr
OXYGENATED-CHLORINATED HYDROCARBON				
Chlordecone (Kepone®)	1.5 to 2.0	5×10^3	very stable	high at 1 ppb or less
Dichlone	.1	5×10^3		
Dicofol (Kelthane®)	ins	1×10^4		high
Dieldrin	.186	1×10^4	T/2 1-7 yr	100% - 8 wks
Endosulfan	<1	5×10^3		30% - 2 wks 5% - 4 wks
Endrin	.23	1×10^4	T/2 4-8 yr	100% - 8 wks
Methoxychlor	.62	1×10^4	T/2 200 d	20 - 38 wks
Tetradiflon	200 at 50°C	5×10^4		
ORGANOPHOSPHATES				
ALIPHATIC DERIVATIVES				
Acephate	very	25		
Demeton	6.6	5×10^2		
Dichlorovos	1.0%	50		62 d at 20°C
Dicrotophos	misc	50		
Dimethoate	2-3%	25	T/2 122 d	85% - 4 wks
Dioxathion	ins	1×10^2		
Disulfoton	25	1×10^2	T/2 290 d	
Ethion	1	5×10^2		
Ethoprop	ins	50		
Malathion	145	1×10^2	1 wk	10-25% - 2 wks 0-10% - 4 wks
Methamidophos	9%	10		
Mevinophos	misc	50		
Monocrotophos	misc	25		100% - 4 wks
Naled	slightly	50		
Oxydemeton-Methyl	300	1×10^2	T/2 26 d	
Phorate	50	5×10^2	2 wk	
Phosphamidon	misc	50		
TEPP	misc	50		T/2 7-8 hr
Trichlorfon	13%	10	T/2 140 d	detected at 256 d
HETEROCYCLIC DERIVATIVES				
Azinphos-Ethyl	ins	1×10^2		
Azinphos-Methyl	33	1×10^2	T/2 20 d	T/2 30 d at pH 9
Chlorofenvinphos	145	5×10^2		
Chlorpyrifos	20	50	T/2 29 d	
Coumaphos	1.5			
Diazinon	40	50	12 wks	50% - 1 wk
Methidathion	240	50		
Phosalone	ins	5×10^2		
Phosmet	25	5 x 102		
Thionazin	1140			

TABLE B.3. (contd)

	Solubility (mg/l)	Kd	Soil Persistence	Water Persistence
PHENYL DERIVATIVES				
Carbophenothion	2	1×10^3		
Chlorothion®	40	2×10^2	T/2 - 36 d	
Crotoxyphos	110	1×10^2		
Crufomate	ins	1×10^2		
Dicapthon	35	5×10^2		
EPN	100 - 11%	1×10^3		
Famphor	slightly	2×10^2		
Fenthion	55	5×10^2		50% - 2 wks 10% - 4 wks
Fonofos	13	2×10^2		
Parathion	20-24	5×10^2	7-20 d	50% - 2 wks 30% - 4 wks
Parathion-Methyl	50-60	3×10^2	2-60 d	11% - 2 wks ~0% - 4 wks
Ronnel	40	2×10^2		
Stirofos	11	2×10^2		
Temephos (Abate®)	ins			
PHENOALKANOATES				
ALIPHATIC ACIDS AND ESTERS				
Dalapon	50%	0.2	15-30 d	2-3 d
Glyphosate	1120 mg/l	0.2	150 d	
Trichloracetic acid (TCA)	83%	0.2	20-70 d	
AROMATIC ACIDS AND ESTERS				
Bifenox	.35	0.5-1	40-60 d	
Chloramben	700	0.5-1	40-60 d	
Chlorthal-Dimethyl (DCPA)	.5	0.5-1	400 d	
Dicamba	4500-7918	0.5-1	2 months	
Endothall	21%	0.2		50% - 1 wk 10% - 2 wks
Fenac	200	0.5-1	350-700 d	
Naptalam	200	0.5-1	20-60 d	
Picloram	430	0.5-1	550 d	
Propargite	ins	0.5-1		
PHENOXY COMPOUNDS				
2,4-D	620 at 25°C	1.0	10-30 d	1% in 30 d
Dinoseb	52	10	15-30 d	
Erbon	ins	1×10^2		
MCPA	27%	1.0	30-180 d	
Silvex	140	2.0		
2,4,5-7	140	2.0	5 months	
PHENYLAMIDES				
AMINES AND ANILINES				
Alachlor	240	50	40-70 d	
Bensulide	25-50	5	10 months	
CDAA	2%		20-40 d	
Diphenamid	260	1×10^2	90-180 d	
Pronamide	15	50	60-270 d	
Propachlor	700	50	30-50 d	
Propanil	500	10	1-3 d	
NITROANILINES				
Benfluralin	.5	5×10^2	120-150 d	
Butralin		5×10^2	90-120 d	
Dinitramine	1	50	90-120 d	
Fluchloralin	~70	1×10^2		

TABLE B.3. (contd)

	Solubility (mg/l)	Kd	Soil Persistence	Water Persistence
Nitralin	.6	50	moderate	
Phenoxalin	.5	1×10^3		
Profluralin	.1	5×10^2	320-640 d	
Trifluralin	1-24	5×10^2	120-180 m	
UREAS				
Chlorbromuron	50	2×10^2		
Chloroxuron	3.7	5×10^2	300-400 d	
Diuron	42	1×10^2	200-500 d	3 months
Fenuron	3850	10	30-270 d	60% - 2 wks 20% - 4 wks
Fluometuron	90	20		
Linuron	75	1×10^2	120 d	20% - 4 wks none - 8 wks
Monuron	230	50	1250-350 d	40% - 2 wks 30% - 4 wks
CARBAMATES				
Aminocarb	slightly	1×10^2		60% - 2 wks 10% - 4 wks
Benomyl	ins	10		
Bufencarb	100	5×10^2	16 wks	
Carbaryl	40-99	5×10^2	T/2 8 days	5% - 2 wks 0% - 4 wks
Carbofuran	700	5×10^2		
Chlorpropham	88-108	1×10^2	120-260 d	
Karbutilate	325	2		
Methiocarb	ins	1×10^2		
Methomyl	5.8%	5		
Mexacarbate	100	1×10^2		15% - 2 wks 0% - 4 wks
Propham	250	50	20-60 d	
Propoxur	2000	1×10^2		50% - 2 wks 30% - 4 wks
THIOCARBAMATES				
Butylate	15-300	5×10^2	40-80 d	
EPTC	370	1×10^2	30 d	
Molinate	800	50	80 d	
Thiram	30	5×10^2		
Vernolate	90	1×10^2	50 d	
TRIAZINES AND TRIAZOLES				
Ametryne	185	8	30-90 d	
Amitrole	28% at 25’C	1	15-30 d	
Atrazine	33 at 27°C	5	300-500 d	
Cyanazine	160-171	3		
Metribuzin	1200	1	150-200 d	
Prometon	677-750	8	>400 d	
Propazine	8.6	1	200-400 d	
Simazine	5	6	200-400 d	
MISCELLANEOUS				
BOTANICALS				
Allethrin	ins	1×10^4		
Pyrethrum/ Pyrethrin (synthetic)	ins	1×10^4		moderate
Rotenone	slight	1×10^3		decomposes readily

TABLE B.3. (contd)

	Solubility (mg/l)	Kd	Soil Persistence	Water Persistence
ARSENICALS				
CMA	2%	0.2		
DSMA	4%	0.2		
MSMA	2.8%	0.2		
DIAZINES-URACILS				
Bentagon	500	0.2		
Bromacil	815	5	T/2 5-6 m	
Pyrazon	300-400	30	30-60 d	
Terbacil	710	50	700 d	
DIPYRIDINUMS				
Diquat	7%	5×10^3	>500 d rapid inactivation	7-27 d
Paraquat	completely	5×10^3	>500 d >2 yr in mud	7-14 d
CYANATES				
Chlorothalonil	.6	50		
Dichlobenil	1.8%	20	60-180 d	2-3 m
METALOIDS				
Copper Napthalate		5×10^2		
Mancozeb	ins	5		
OTHER				
Acrolein	moderate	0.2		
Captan	>.5	30		
Carboxin	170	10		
Difolatan	ins	50		
Dodine	6300	0.5		
Methazole	1.5	5		
Methyl Bromide	1.75%	10		
Norflurazon	28	50		

REFERENCES

American Chemical Society. 1969. *Cleaning Our Environment: The Chemical Basis for Action*. Washington, DC.

American Fisheries Society. 1970. *A List of Common and Scientific Names of Fishes from the United States and Canada*. R. M. Bailey (Chairman), Third Edition, Special Publications, No. 6, Washington, DC.

Alabaster, J. S. 1969. "Survival of Fish in 164 Herbicides, Insecticides, Fungicides, Wetting Agents and Miscellaneous Substances." *International Pest Control*, March/April, pp 29-35.

Allison, D. T., and R. O. Hermanutz. 1977. *Toxicity of Diazinon to Brook Trout and Fathead Minnows*. EPA-600/3-77-060, U.S. Environmental Protection Agenty, Duluth, MN.

Battelle's Columbus Laboratories. 1971. *Water Quality Criteria Data Book - Volume 3*. 18050 GWV05/71. U.S. Environmental Protection Agency, Washington DC.

Bond, C. E., R. H. Lewis and J. L. Fryer. 1960. *Toxicity of Various Herbicidal Materials to Fish*. R. A. Taft. San. Eng. Cen. Tech. Rept. W60-3:96-1-1.

Bridges, W. R. and O. B. Cope. 1965. "The Relative Toxicities of Similar Formulations of Pyrethrum and Rotenone to Fish and Immature Stoneflies." *Pyrethrum Post*, 8:3-5.

Brungs, W. A., R. W. Carlson, W. B. Horning II, J. H. McCormick, R. L. Spehar and J. D. Yount. 1978. "Effects of Pollution on Freshwater Fish." *Journal of Water Control Federation*, 50(6):1582-1637.

Burdick, G. E., H. J. Dean, and E. J. Harris. 1964. "Toxicity of Aqualin to Fingerling Brown Trout and Bluegells." *N.Y. Fish and Game J.*, 11(2):106-114.

Call, D., L. Brooke, and R. Kent. 1979. *Estimates of No-effect Concentration of Selected Pesticides in Freshwater Organisms*. Third Quarterly Progress Report to EPA, 1 January through 31 March 1979. U.S. EPA Grant No. R-806196-01. University of Wisconsin, Superior, WI.

Cardwell, R. D., D. G. Foreman, T. R. Payne, D. J. Wilbur. 1977. *Acute and Chronic Toxicity of Chlordane to Fish and Invertebrates*. EPA 600/3-77-019, U.S. Environmental Protection Agency, Duluth, MN.

Cairns Jr., J. and A. Scheier. 1964. "The Effect Upon the Pumpkinseed Sunfish *Lepomis gibbosus (Linn.)* of Chronic Exposure to Lethal and Sublethal Concentrations of Dieldrin." *Notulae Natur*, (370)1-10.

Carlson, A. R. 1972. "Effects of Long-Term Exposure to Carbaryl (Sevin) on Survival, Growth, and Reproduction of the Fathead Minnow, (*Pimephales promelas*)." *J. Fisheries Research Board of Canada*, 29(5):583-587.

Carlson, C. A. 1966. "Effects of Three Organophosphorus Insecticides on Immature Hexagenia and Hydropsyche of the Upper Mississippi River." Trans. American Fisheries Society. 95(1):1-5.

Cope, O. B. 1965. "Contamination of the Fresh-Water Ecosystem by Pesticides." Journal of Applied Ecology, 3(Supplement):33-44.

Cope, O. B. 1965. "Sport Fishery Investigations." In The Effects of Pesticides on Fish and Wildlife." U.S. Fish and Wildlife Service, Circ. 226:51-63, U.S. Department of the Interior, Washington, DC.

Cope, O. B. 1963. "Sport Fishery Investigation." Pesticide-Wildlife Studies, A Review of Fish and Wildlife Service Investigations During 1961 and 1962. U.S. Fish and Wildlife Service, Circ. 167:26-42, U.S. Department of the Interior, Washington, DC.

Crosby, D. G. and R. K. Tucker. 1966. "Toxicity of Aquatic Herbicides to Daphnia magna." Science, 154:289-291.

Donigian Jr., A. S. and H. H. Davis Jr. 1977. Agricultural Runoff Management (ARM) Model User's Manual: Versions I and II. Prepared for the U.S. Environmental Protection Agency, Athens, GA.

Eaton, J. G. 1970. "Chronic Malathion Toxicity to the Bluegill (Lepomis macrochirus rafinesque." Water Research, 4:673-684.

Environmental Protection Agency. 1972. Effects of Pesticides in Water - A Report to the States. PBB222-320, Prepared for Office of Water Resources Research by NTIS, U.S. Department of Commerce.

Environmental Protection Agency. 1976. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, DC.

Ferguson, D. E., D. T. Gardner and A. L. Lindley. "Toxicity of Dursban to Three Species of Fish." Mosquito News, 26(1):80-82.

Gaufin, A. R., L. D. Jensen, A. V. Nebeker, Thomas Nelson, and R. W. Teel. 1975. "The Toxicity of Ten Organic Insecticides to Various Aquatic Invertebrates." Water and Sewage Works.

Gilderhus, P. A. 1967. "Effects of Diquat on Bluegills and Their Food Organisms." The Progressive Fish-Culturist, 29:67-74.

Gillett, J. W. (ed.) 1969. "The Biological Impact of Pesticides." In the Environment Proceedings of the Symposium, August 18-20, 1969 at Oregon State University, Corvallis, OR.

Guenzi, W. D. (ed.) 1974. Pesticides in Soil Water. Soil Science Society of America, Inc., Madison, WI.

Henderson, C. and Q. H. Pickering. 1958. "Toxicity of Organic Phosphorus Insecticides to Fish." Trans. American Fisheries Society, 87:39-51.

Henderson, C., Q. H. Pickering and E. M. Tarzwell. 1959. "Relative Toxicity of Ten Chlorinated Hydrocarbon Insecticides to Four Species of Fish." Trans. American Fisheries Society, 88:23-32.

Hermanutz, R. O., L. H. Mueller, and K. D. Kempfert. 1973. "Captan Toxicity to Fathead Minnows (Pimephales promelas) Bluegills (Lepomis macrochirus) and Brook Trout (Salvelinus fontinalis)." J. Fisheries Research Board Canada, 30:1811-1817.

Hughes, J. S. and T. D. James. 1962. "Comparative Toxicity of Bluegill Sunfish to Granular and Liquid Herbicides." Proceedings Sixteenth Annual Conference Southeast Game and Fish Commissioners, pp 319-323.

Hurtig, H. 1972. "Long-Distance Transport of Pesticides." Environmental Toxicology of Pesticides, Academic Press, New York, NY.

Jarvinen, A. W., M. J. Hoffman, T. W. Thorslund. 1976. Toxicity of DDT Food and Water Exposure to Fathead Minnows. EPA-600/3-76-114, U.S. Environmental Protection Agency, Duluth, MN.

Jensen, L. D. and A. R. Gaufin. 1964. "Long-Term Effects of Organic Insecticides on Two Species of Stonefly Naiads." Trans. American Fisheries Society, 93(4):357-363.

Jensen, L. D. and A. R. Gaufin. 1966. "Acute and Long-Term Effects of Organic Insecticides on Two Species of Stonefly Naiads." J. Water Pollution Control Federation, 38(8):1273-1286.

Johnson, D. W. 1968. "Pesticides and Fishes, A Review of Selected Literature." Trans. American Fisheries Society, 97(4):398-424.

Katz, M. 1961. "Acute Toxicity of Some Organic Insecticides to Three Species of Salmonids and to the Threespine Stickleback." Trans. American Fisheries Society, 90(3):264-268.

Katz, M., D. L. Pederson, M. Yoshinaka and D. Sjolseth. 1969. "Effects of Pollution on Fish Life." J. Water Pollution Control Federation, 41(6).

Kemp, H. T., R. L. Little, V. L. Holman, and R. L. Darby. 1973. Water Quality Criteria Data Book - Vol. 5 - Effects of Chemicals on Aquatic Life. U.S. Environmental Protection Agency. NTS-PB-234 435.

Kenaga, E. E. 1974. "2,4,5-T and Derivatives: Toxicity and Stability in the Aquatic Environment." Down to Earth, 30(3):19-25.

Korn, S. and R. Earnest. 1974. "Acute Toxicity of 20 Insecticides to Striped Bass, Morone saxatilis." California Fish and Game, 60:128.

Lane, C. E. and R. J. Livingston. 1970. "Some Acute and Chronic Effects of Dieldrin on the Sailfin Molly, Poecilis latipinna." Trans. American Fisheries Society, 3:489-495.

Macek, K. J. and W. A. McAllister. 1970. "Insecticide Susceptibility of Some Common Fish Family Represenatives." Trans. American Fisheries Society, 1:20-27.

Macek, K. J., D. F. Walsh, J. W. Hogan and D. D. Holz. 1972. "Toxicity of the Insecticide Dursban to Fish and Aquatic Invertebrates in Ponds." Trans. American Fisheries Society, 3:420-427.

Macek, K. J., K. S. Buxton, S. K. Derr, J. W. Dean and S. Sauter. 1976. Chronic Toxicity of Lindane to Selected Aquatic Invertebrates and Fishes. EPA-600/3-76-046, U.S. Environmental Protection Agency, Duluth, MN.

Macek, K. J., K. S. Buxton, S. Sauter, S. Gnilka and J. W. Dean. 1976. Chronic Toxicity of Atrazine to Selected Aquatic Invertebrates and Fishes. EPA-600/3-76-047, U.S. Environmental Protection Agency, Duluth, MN.

Macek, K. J., M. A, Lindberg, S. Sauter, K. S. Buxton and P. A. Costa. 1976. Toxicity of Four Pesticides to Water Fleas and Fathead Minnows. EPA-600/3-76-099, U.S. Environmental Protection Agency, Duluth, MN.

Mauck, W. L., L. E. Olson and J. W. Hogan. 1977. "Effects of Water Quality on Deactivation and Toxicity of Mexacarbate (Zectran) to Fish." Arch. Environmental Contamination and Toxicology, 6:385-393.

Mauck, W. L., and L. E. Olson. 1976. "Toxicity of Natural Pyrethrins and Five Pyrethroids to Fish." Archives of Environmental Contamination and Toxicology, 4:18-29.

Mayer Jr., F. L., P. M. Mehrle Jr. and W. P. Dwyer. 1977. Toxaphene Chronic Toxicity to Fathead Minnows and Channel Catfish. EPA-600/3-77-06A, U.S. Environmental Protection Agency, Duluth, MN.

Mayer Jr., F. L., P. M. Mehrle Jr. and W. P. Dwyer. 1975. Toxaphene Effects on Reproduction, Growth, and Mortality of Brook Trout. EPA-600/3-75-013, U.S. Environmental Protection Agency, Duluth, MN.

McCorkle, F. M., J. E. Chambers and J. D. Yarbrough. 1977. "Acute Toxicities of Selected Herbicides to Fingering Channel Catfish, Ictalurea punctatus." Bulletin of Enviromental Contamination and Toxicology, 18(3):267-270.

McKim, J. M. 1977. "Evaluation of Tests with Early Life Stages of Fish for Predicting Long-Term Toxicity." J. Fisheries Research Board of Canada, 34(8):1148-1154.

McKim, J. M., D. A. Benoit, K. E. Biessinger, W. A. Brungs and R. E. Siefert. 1975. "Effects of Pollution on Freshwater Fish." J. Water Pollution Control Federation, 47(6):1711-1768.

Miller, M. W. and G. G. Berg (Eds.) 1969. Chemical Fallout Current Research on Persistent Pesticides. Charles C. Thomas Publishing Co., Springfield, Ill.

Mitchell, L. E. 1966. "Pesticides: Properties and Prognosis." Organic Pesticides in the Environment. Advances in Chemistry Series 60, American Chemical Society, Washington, DC.

Mount, D. I. and C. E. Stephan. 1967. "A Method for Establishing Acceptable Toxicant Limits for Fish - Malathion and the Butoxyethanol Ester of 2,4,-D." Trans. American Fisheries Society, 97:185-193.

Mount, D. I. 1977. "An Assessment of Application Factors in Aquatic Toxicology." In Recent Advances in Fish Toxicology: A Symposium. EPA-600/3-77-085, U.S. Environmental Protection Agency, Corvallis, OR.

Reese, C. D. (Project Officer) 1972. "Pesticides in the Aquatic Environment." U.S. Environmental Protection Agency, Washington, DC.

Pickering, Q. H. and C. Henderson. 1966. "The Acute Toxicity of Some Pesticides to Fish." The Ohio Journal of Science, 66(5):508-513.

Pickering, Q. H., C. Henderson and A. E. Lemke. 1962. "The Toxicity of Organic Phosphorus Insecticides to Different Species of Warmwater Fishes." Trans. American Fisheries Society, 91:175-184.

Pimentel, D. 1971. Ecological Effects of Pesticides on Non-Target Species. Executive Office of the President, Office of Science and Technology, Washington, D.C.

Rudd, R. L. 1964. Pesticides and the Living Landscape. University of Wisconsin Press, Madison, WI.

Sanborn J. R., B. M. Francis and R. L. Metcalf. 1977. The Degration of Selected Pesticides in Soil: A Review of the Published Literature. EPA-600/9-77-022, U.S. Environmental Protection Agency, Cincinatti, OH.

Sanders, H. O. 1969. Toxicity of Pesticides to the Crustacean Gammarus lacustris. Bureau of Sport Fisheries and Wildlife, Tech. Paper No. 25, U.S. Department of the Interior, U.S. Government Printing Office, Washington, DC.

Sanders, H. O. 1970. "Toxicities of Some Herbicides to Six Species of Freshwater Crustaceans." J. Water Pollution Control Federation, 42(8):1544-1500.

Sanders, H. O. 1972. The Toxicities of Some Insecticides to Four Species of Malocostrocan Crustacea. Bureau of Sport Fisheries and Wildlife, Tech. Paper No. 66, U. S. Government Printing Office, Washington, D.C.

Sanders, H. O. and O. B. Cope. 1966. "Toxicities of Several Pesticides to Two Species of Cladocerans." Trans. American Fisheries Society. 95(2):165-169.

Sanders, H. O. and O. B. Cope. 1968. "The Relative Toxicities of Several Pesticides to Naiads of Three Species of Stoneflies." Limnology and Oceanography, 13(1):112-117.

Schoettger, R. A. 1970. Toxicology of Thiodan in Several Fish and Aquatic Invertebrates." Bureau of Sport Fisheries and Wildlife, Investigations in Fish Control, Paper 35, U.S. Department of the Interior, Washington, DC.

Snarski, V. M. and F. A. Puglisi. 1976. Effects of Aroclor 1254 on Brook Trout, Salvelinus fontinalis. EPA-600/3-76-112, U.S. Environmental Protection Agency, Duluth, MN.

Solon, J. M. and J. H. Nair III. 1970. "The Effect of a Sublethal Concentration of LAS on the Acute Toxicity of Various Phosphate Pesticides to the Fathead Minnow, Pimephales promelas rafinesque." Bulletin Envir. Contam. and Toxico., 5(5):408-413.

Spacie, A. 1975. "Acute and Chronic Parathion Toxicity to Fish and Invertebrates." U.S. Environmental Protection Agency, Washington, DC.

Stewart, B. A., D. A. Woolhiser, W. H. Wischmeier, J. H. Caro and M. H. Frere. 1976. Control of Water Pollution for Cropland: Volume I - An Overview. Agricultural Research Service, U.S. Department of Agriculture, Washington, DC.

Surber, E. W. and Q. H. Pickering. 1962. "Acute Toxicity of Endothal, Diquat, Hyamine, Dalapon, and Silvex to Fish." The Progessive Fish Culturist, 24:164-171.

U.S. Department of Health, Education, and Welfare, Pesticides and Their Relationship to Environmental Health (Parts I & II). H.U.D. Secretary's Commission, Washington D.C.

Walker, C. R. 1964. "Toxicological Effects of Herbicides on the Fish Environment." Water and Sewage Works, 3(3).

Water Quality Criteria. 1972. Committee on Water Quality Criteria, EPA-R3-73-033, U.S. Environmental Protection Agency, Washington, DC.

Weed Science Society of America. 1970. Herbicide Handbook. Second Edition, W. F. Humphrey Press, Inc., New York, NY.

Weed Science Society of America. 1979. Herbicide Handbook. Fourth Edition. W. F. Humphrey Press, Inc., New York, NY.

Wilber, C. G. 1969. The Biological Effects of Water Pollution, Charles C. Thomas Publishing Co., Springfield, IL.

Wilson, D. C. and C. E. Bond. 1969. "The Effects of the Herbicides Diquat and Dichlobenil (Casoron) on Pond Invertebrates, Part 1 - Acute Toxicity." Trans. American Fisheries Society, 98(3):438-443.

APPENDIX C

DISTRIBUTION COEFFICIENTS OF ORGANIC PESTICIDES IN AQUATIC ECOSYSTEMS*

INTRODUCTION

This report considers certain aspects of the distribution of organic pesticides between water and solid abiotic phases in natural aquatic (fresh water) ecosystems. This study was performed for Battelle Pacific Northwest Laboratory in support of a larger study of the mobility and transport of the pesticides in natural riverine ecosystems.

The report considers three main points:

1. A discussion of the molecular and environmental parameters that affect the distribution of the pesticides in natural systems,
2. A discussion of mathematical expressions useful in describing the distribution (or partitioning) of the pesticides between the aqueous and solid phases, and
3. The presentation of estimated distribution coefficients for the specific pesticides of interest in this study.

The first two points are considered in Part 1 of this report, while the estimated distribution coefficients are presented in tabular form in Part 2.

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*Submitted to Battelle, Pacific Northwest Laboratories, by R.N. Dexter, URS Company, as final report of the services provided under consultant agreement B-62522-B-L.

PART 1: ADSORPTIVE EQUILIBRIA

The discussion below is based both on a consideration of general partitioning theory and a review of pertinent literature concerned with adsorption in natural systems. Many of these points considered can be found in reviews by Hamaker and Thompson, 1972; Zettlemoyer and Micale, 1971; and Bailey and White, 1970.

ADSORPTION

For the discussion below, equilibrium between the adsorbed and solution phases is assumed. At this point a balance of forces is established and the chemical potential or activity of the sorbate (pesticide) must be the same in the solution and on the surface of the solid matrix. A consideration of the intermolecular interactions which give rise to these chemical potentials is then informative in defining the behavior to be expected for different types of sorbates and in determining the parameters of natural systems which can be expected to affect the chemical potentials and thus the adsorptive equilibria.

Aqueous Solution

It is well recognized that liquid water is anomalous in its behavior compared to similar chemical species. This results primarily from the high polarity of the water molecules which produces strong internal hydrogen bonding. The dipole also generates strong electrostatic attractive forces between water molecules and ionizable and polar moieties of organic and inorganic compounds.

At the same time, the hydrogen bonding among water molecules leads to considerable internal structure in liquid water. As a result, the introduction of solute forces the rearrangement of the normal structure of liquid water in the vicinity of the solute molecules. This restructuring generally requires an energy contribution to compensate for the entropy change. In a practical sense, this acts as a repulsive force opposing the accommodation of the solute. This apparent repulsion from water can force strong associations between certain molecules and is referred to as hydrophobic interaction (or hydrophobic bonding). As a general rule, the entropic contribution and thus the strength of the hydrophobic interaction is a function of the effective size of the solute molecule in solutions (Franks, 1975).

The activity, then, is a function of both the concentration and the balance between the attractive electrostatic forces and the entropy-generated repulsion. Solute compounds can thus he ranked based on their size and their ability to participate in electrostatic interactions. For example, totally ionized inorganic solutes are small species with high charge densities leading to low aqueous activity coefficients as reflected in their relatively high solubilities. On the other end of the scale, non-polar hydrocarbons interact only through relatively weak van der Waals interactions. For these compounds, the hydrophobic interaction is strong resulting in high activity coefficients and low solubilities. The solubilities and activity coefficients of hydrocarbons correlate well with the size of these molecules (Tsonopolus and Prausnitz, 1971; Frank and Evans, 1945).

The majority of organic pesticides fall somewhere between these extremes. Most have some charge localization arising from heteroatoms in the structure, particularly oxygen, and some have ionizable hydrogens. For these compounds, the interactions with water are complex functions of both the electrostatic and hydrophobic interactions. Within limits, the relative activities of a group of compounds with the same polar moiety will correlate with the size of the non-polar substituents. Conversely, from such correlations, the absolute contribution of the polar moiety can be estimated to generate empirical additivity rules for ranking other similar compounds (Tsonopolus and Prausnitz, 1971).

These activity relationships are complicated by two factors. First, substitution of various moieties on the parent molecule can have secondary impacts, primarily by withdrawing or contributing electrons to polar sites or sites with active hydrogens. For example, monosubstituted nitrophenols as a group are much less soluble than phenol (solubility = 93 g/l). However, _o_- nitrophenol (solubility = 2 g/l) is nearly an order of magnitude less soluble than the _m_- or _p_- substituted compounds (_m_- nitrophenol, solubility - 14 g/l; _p_- nitrophenol, solubility - 17 g/l) (Morrison and Boyd, 1966, pp. 790-792). Second, natural waters are not pure, but are rather complex and variable solutions. The principal parameters affecting the activity of dissolved species (particularly organics) are pH, ionic strength and type of ions, the quantity and nature of dissolved (and colloidal) organic matter, and temperature.

pH

The pH controls the speciation of ionizable acid and base groups; the ionized forms interact more strongly with water, e.g., are more soluble.

Ionic Strength

The ions of natural dissolved salts generally tend to increase the normal ordering within the liquid such that the ability to accommodate organic compounds in reduced ("salting out") and hydrophobic interactions are increased.

Dissolved Organic Matter

Natural dissolved organic matter (DOM) consists principally of refractory polyelectrolytes resulting from the degradation of biological materials (Christman and Minear, 1971). The DOM form stable solutions which can scavenge and suspend pesticides either through electrostatic (ion-ion, ion-dipole, or ligand) interactions or, for less polar materials, through hydrophobic interactions with non-polar sites in the DOM matrix. The net result is to reduce the dissolved concentration (and thus the activity) of the pesticides in solution without necessarily decreasing the (analytically determined) concentration. The interactions between DOM and pesticides may in turn be altered by changes in either pH or ion content, which will affect the degree of ionization, the effective charge density, and the three dimensional structure of the DOM molecules.

Temperature

In all cases, interactions are affected by temperature changes. In general, as the temperature increases the activity decreases for polar species while it may increase for non-polar compounds. Over the normal range of temperature fluctuations exhibited by natural systems, the effect is small for most compounds.

Surface Interactions

Interactions between the sorbate pesticide compounds and sites on the absorbent solid matrix are entirely electrostatic (excluding chemisorption) and primarily a function of the polarity of the sorbate molecule, ranging from weak van der Waals to ion-ion bonding. Natural soil and and sediment matrices are either inorganic mineral grains, usually coated or aggregated with organic polyelectrolytes, or detrital organic particles (Kononova, 1966). In either case, numerous sites are available which carry weak to strong charge localizations, usually with a net negative charge exhibited by the whole particle (Neihof and Loeb, 1972). To the extent that adsorption is a surface phenomena, smaller particles will show higher mass-normalized concentrations of pesticide due to their greater specific surface area (Leland, *et al.*, 1973).

In addition, many inorganic particles in natural environments contain pores and interstices between crystallization planes which allow sorbate molecules to diffuse into the interior of the particle. (Knight and Tomlinson, 1970.) Similarly, pesticides may be capable of diffusing into the interior of detrital organic particles in a fashion similar to passive diffusion through biological membranes. In both cases, quantitative differences may exist in the interactions between the sorbate and the readily accessible surfaces of the particles and the interior sites. Further, exchange rates with the interior would be expected to be much slower than with surface sites.

Both pH and ionic strength will affect the characteristics of the surfaces. The pH effectively gives a measure of the H^+ or OH^- ions available to satisfy specific acidic or basic moieties on the surface, while counterions act less specifically to satisfy residual charges sites. Due to these factors, rather complex adsorption trends may develop resulting from competitive ion exchange, ligand, and dipole interactions between surface sites, natural ions, and polar pesticides. Non-polar pesticides would not be significantly affected by these changes.

One factor which must be considered, but is not often recognized, is that in adsorption from aqueous solutions the water molecules themselves interact with the surface and are in competition for polar sites with all other adsorbates. Even in cases where the relative binding strengths of water molecules may be weak, the predominance of water molecules in natural systems (i.e., dilute solutions) makes them important contributors to the overall process.

The factors discussed above will affect the adsorption are summarized in Table 1. Based on a consideration of the dominant types of interactions (hydrophobic or electrostatic).

Table 1

SUMMARY OF ADSORPTION INTERACTIONS IN NATURAL AQUEOUS ENVIRONMENTS

TYPE OF INTERACTION	EFFECTOR VARIABLES		
		ENVIRONMENTAL	
	MOLECULAR	AQUEOUS PHASE	SOLID PHASE
Hydrophobic	Molecular Size	Ionic Strength, DOM* Temp	Surface Chemistry Temp
Electorstatic	Charge Density, Polarizability, Acid/Basic Moieties	Ionic Strength, pH, DOM* Temp	Surface Chemistry, Ionic strenght, pH, Temp

*DOM acts to reduce the dissolved concentration.

EQUILIBRIUM RELATIONSHIPS

Theoretical Basis

To provide useful data for predicting the distribution behavior it is desireable to establish adsorption equilibrium relationships between the concentrations in the aqueous and sorbed phases, i.e., adsorption isotherms. The primary intent is to obtain mathematical expressions, hopefully not overly complex, for the isotherms.

A number of isotherm equations are available which have been examined as to their applicability to adsorption from solution in natural systems. These include the Freundlich, Langmuir and Brunauer-Emmett-Teller (BET) isotherms. Of these only the last two have any coherent theoretical basis (Adamson, 1976). Each is based on different assumptions as to the processes leading to adsorption and each finds use in explaining different adsorption systems. It should be noted that most of the theoretical studies in developing and justifying these expressions has relied on well characterized, vapor phase systems (Adamson, 1976).

Due to the strong and specific binding arising from ion-ion interactions, it would be anticipated that metal salt pesticides would be the most likely to follow a Langmuir type isotherm. Conversely, adsorption of non-polar organics, for which hydrophobic interactions perdominate, would be expected to include multilayer formation at higher concentrations and thus more likely to be represented by a BET type isotherm. Similarly, BET would be a likely model isotherm for organic pesticides of intermediate polarity since electrostatic behavior could predominate at low concentrations, but hydrophobic interactions would undoubtedly be important as the aqueous solution approaches saturation.

At the same time, neither Langmuir nor BET isotherm expressions have not been utilized to any great extent with natural systems. The primary argument has been that natural adsorbents do not present a homogenous surface (constant adsorption energies independent of surface coverage) which is required for these equations to be applicable (Adamson, 1976). As a result, the most frequently encountered expression is the Freundlich isotherm, which while having no theoretical basis, is a semi-logarithmic type expression with empirically determined parameters and has been used to fit many observed adsorption relationships.

However, the present body of data which has popularized the Freundlich isotherm is not free from criticism. First, the perponderance of studies have been performed by soils chemists and engineers primarily concerned with the factors controlling the biocidal activity of agricultural pesticides. In the majority of these studies, the aqueous concentrations of pesticides utilized were often much higher than normally encountered in natural systems, the experimental levels often approaching or even exceeding the solubilities of the test compounds (Hamaker and Thompson, 1972). In some cases this was done to maintain detectable levels of the pesticides in all phases; in other cases, levels approximating field application levels were used.

In addition most studies have examined a relatively limited range of aqueous concentrations compare to what is encountered in natural systems. With this limited experimental base, it is difficult to insure that the data can be extrapolated to either higher or lower concentrations or that the isotherm expression is truly representative of the adsorption behavior.

At higher concentrations, particularly as the solubility is approached, a number of effects which can give rise to non-linear isotherms can occur. 1) At higher concentrations, solute-solute intermolecular interactions may increase particularly for more hydrophobic compounds. This results in a decrease in the activity coefficient and thus a non-linear relationship between the aqueous activity and the concentration such that adsorption would be relatively diminished (other factors being invariant), i.e, 1/n<1 in terms of the Freundlich expression. 2) For polar and ionic pesticides, as the particle surface coverage increases, all sites of strong electrostatic interaction can be occupied, resulting in decreasing relative adsorption as the aqueous concentration increases, i.e., 1/n<1, or Langmuir type behavior. 3) For hydrophobic molecules, increased aqueous concentrations can lead to relatively increased adsorption either due to "condensation" on the surface, forming multiplyers (BET type adsorption), or due to self-adsorption by increasing the area of preferred, low-polarity adsorption sites. In either case, 1/n>1.

All of these effects are greatly diminished at reduced concentrations when the opportunity for solute-solute interactions either in solution or on the surface and the number of occupied surface sites are all minimal.

It can be argued convincingly that these conditions are most likely in natural systems (except, of course, agricultural land receiving direct applications), both on the basis of measured residue levels which are routinely observed at very low concentrations and by considering that the residue undoubtedly undergo a number of adsorption-desorption steps during mobilization from the site of application. Under these conditions, it would seem apparent that, since the probably sources of non-linear adsorption are virtually eliminated, 1/n should approach unity for those systems where the Freundlich isotherm is applicable. Note also that at low concentrations both the Langmuir and BET isotherms reduce to linear forms.

A further criticism of the available data is concerned with the interpretation of the kinetics of the experimental results. Where rate information is available, the usual behavior observed is rapid initial uptake (<24 hours) followed by slow uptake which increases the adsorbed concentration by about 10% over a period of one to two months. Desorption experiments performed immediately after adsorption generally yield reversible adsorption isotherms (at least when the aqueous concentrations of the solute are below saturation). However, desorption and residue recovery experiments performed after long equilibration periods have often, but not always, shown a portion of the adsorbed residues to be more strongly retained in the solid matrix than would be indicated from the adsorption isotherm (Hamaker and Thompson, 1972, pp. 92-97).

Two alternatives have been considered to explain this behavior: 1) chemisorption (Huangand Liao, 1970) and 2) migration of the residues either to stronger binding sites not entirely occupied during the initial adsorption, or to the interior of the particle. (Saha, et al., 1969). Chemisorption seems unlikely since the residues can be recovered in unaltered form, and considering the energy requirements which would be required to produce chemical binding without destroying the pesticide molecule. Simple migration to strongly binding surface sites would not seem to require such long periods before their effect would be observed. Obviously, the simplest and most reasonable explanation is the physical migration of the pesticide molecules into the interior of the particle, either through pores and between the crystallization planes of laminar clays (e.g. montmorillonites), or below the surface of organic detrital particles. With organically coated particles, it is possible that the migration of polar and ionic pesticides may also yield inherently stronger binding to the inorganic matrix (Burns and Andrus, 1970). In most cases, however, it appears likely that the slow rates of intraparticle diffusion which would be sufficient to explain the slow desorption and apparent incomplete recoveries.

Of major concern at this point is the implication of these results in estimating the mobility of the pesticide residues in natural systems. The major conclusions that can be drawn are 1) that the majority of experimental K_d values underestimate the actual distribution coefficient applicable in natural systems, and 2) that many of the available desorption studies do not realistically represent the behavior of the residues in natural systems.

In further support of these conclusions is the observation that most studies examining the migration of pesticides in actual field situations indicate that the movement of even relatively soluble herbicides is generally limited and much less than what would be predicted on the basis of laboratory equilibrium or soil leaching experiments.

Natural Systems

The information discussed above should be considered within the framework of natural systems to discern the implication of equilibrium distribution coefficients for predicting environmental mobility associated with the movement of water.

The first situation is the movement of pesticides from the site of initial application, e.g., agricultural land. Two major processes can be defined 1) leaching via percolation through the soil in the groundwater, and 2) direct overland runoff associated with heavy rains or excess irrigation water. The great predominance of soil mass compared to water in groundwater flow indicates that movement of even slightly adsorptive compounds should be very slow. On the other hand, runoff events are rapid with relatively short contact times between the runoff water and the soils in the fields compared to the probable rates of desorption of most compounds. In addition contact with the soil-incorporated residues is minimal, except for contact with that portion of the soil which is itself mobilized by the runoff. In many situations, this latter soil component probably contributes the largest fraction of mobile pesticides, independent of the strength of adsorption of the residues.

As a result of these effects, neither the mass moved nor the distribution between particulate and water fractions of the residues could be expected to be strong functions of distribution coefficients. Rather, both the mass movement and the total concentration of the residues should correlate with the corresponding parameters for suspended soil particles. Such behavior has been noted for storm-generated runoff from experimental plots (Donigian, et al., 1977).

In permanent water bodies (rivers, lakes, etc.), however, the situation is markedly different. Since the residues have already undergone numerous adsorption/desorption steps in traveling to the water body the aqueous concentrations are much reduced compared to levels in agricultural usage. Further dilution normally occurs soon after introduction into the system. The effect should be reduced the pesticide concentrations to the range of linear activity-concentration relationships for the residues in both the aqueous and solid phases, and thus linear distribution coefficients, K_d, should be applicable.

Further, the solid particles are always completely hydrated. Many of the physical effects which can alter the mobility of pesticides in soils as a result of wet/dry cycles are eliminated, e.g., collapse of pores and voids in organic coatings on drying the slow rehydration of interior binding sites, and the swelling of the inter-laminar spaces of clays. It is reasonable that this stability of the solid matrix would tend to eliminate differences in the long term adsorption/desorption behavior and, by keeping intraparticle voids and pores open, facilitate exchange between the solid and aqueous phases. These points would further argue for linear, equilibrium adsorption.

Summary

From the foregoing discussions the following conclusions can be made:

1. The majority of the available adsorption data underestimates the actual strength of the adsorption on solid matrices.

2. The majority of the available data also oversimplifies the equilibrium adsorption relationships.

3. In natural runoff from agricultural land receiving direct application of pesticides, the mobility of any pesticide and its relative distribution in the mobile aqueous and solid phases are predominantly functions of the physical processes taking place, with adsorption-desorption considerations of lesser importance. It is probably not reasonable to apply distribution coefficients or even more complex adsorption isotherms to these situations.

4. In permenant water bodies receiving indirect pesticide inputs, linear adsorption isotherms would be applicable, and the relative distribution should be adequately characterized by a single distribution coefficient, K_d.

PART 2: VALUES OF THE DISTRIBUTION COEFFICIENT, K_d

The estimation of reasonable K_d values for the pesticides of interest in this study is difficult for three reasons. (1) Fundamental physical chemical properties, e.g., solubility, have been determined for only a few of the compounds and even the data which have been reported are not always reliable. (2) Even empirical parameters, such as the octanol-water partition coefficient, which would be suitable for ranking the adsorptability and estimating approximate values for K_d, are not readily available. (3) The adsorption data which have been reported in the literature often suffer from the limitations discussed in Part 1. In addition, the data for a single compound often vary by more than an order of magnitude, reflecting both artifacts of different experimental techniques and real variability resulting from differences in the adsorptive matrix, particularily when comparisons are made between pure clays, natural loams, and natural muck or peat soils.

The K_d values presented below were estimated for an "average" or "normal" freshwater system. The solid matrix is assumed to consist of silty-sand of about 1%.to 3% organic matter. The aqueous phase is assumed to have low total solids, pH of between 7 and 8 and to be unpolluted by large quantities of detrital organic matter.

K_d values for some non-polar (organochlorine) pesticides and related compounds have been predicted previously, based on fundamental physical chemical properties (Dexter and Pavlou, 1978). Such an approach was not viable for this study, however, due in part to the lack of reading available fundamental data for all of the compounds, and in part to the time restraints encountered.

The values presented are, of necessity, fairly rough estimates based on careful consideration of the adsorption coefficients and relative adsorption data available in the literature, and on a consideration of the relative molecular structural contributions to the adsorptive interactions, e.g., molecular size, polarity of heteroatom moieties, number of polar groups, etc. As a first step, the molecular structures were compared and the pesticides within each group ranked according to probable relative adsorption strength. From the previous calculations and from selected literature references, K_d values for some of the pesticides could be estimated with some certainty. By further comparisons of the molecular structures of these "marker" compounds with the ranked pesticides, appropriate K_d values were estimated for natural systems.

The values are presented in tables for each pesticide group with an approximate ranking of the compounds within each group beginning with the highest K_d value.

Each table is followed by a short discussion of the rationale for the estimated K_d values and any available supporting literature data.

ORGANOCHLORINE PESTICIDES

A. Aromatic	K_d
DDT	1×10^5
TDE (DDD)	5×10^4
Tetradiflon	5×10^4
Methoxychlor	1×10^4
Kelthane	1×10^4
Dichlone	5×10^3

B. Aliphatic	
Aldrin	7×10^4
Isodrin	7×10^4
Chlordane	5×10^4
Toxphene	5×10^4
Mirex	5×10^4
Heptachlor	1×10^4
Endrin	1×10^4
Dieldrin	1×10^4
Chlodecone	5×10^3
Endosulfan	5×10^3
Lindane	1×10^3
BHC	1×10^3

Rationale: These compounds by and large are the most easily considered since they contain relatively few polar moieties. As a result adsorption is due primarily to hydrophobic interaction and van der Walls forces. For this reason relative adsorption will be correlated with the molecular size with corrections for polar groups and non-conjugated double bonds. Further, values of K_d can be approximated from theoretical calculations (Dexter and Pavlou, 1978).

Some literature support for the values can be obtained from the literature. Values for K_d for DDT of approximately 1×10^5 have been reported in soils by Shien *et al.* (1974), and Pavlou *et al.* (1974). The value for lindane was reported by Lotse *et al.* (1968) and Boucher and Lee (1972). Values of distribution coefficients for some of the other compounds have been reported, but most appear to be far from a reasonable range (Hamaker and Thompson, 1972).

ORGANOPHOSPHATE PESTICIDES

A. Aliphatic Deriatives	K_d
Ethion	5×10^2
Disulfoton	5×10^2
Counter	5×10^2
Demeton	5×10^2
Phorate	5×10^2
Dioxathion	1×10^2
Malthion	1×10^2
Oxymeton methyl	1×10^2
Dichlorvos	50
Ethoprop	50
Phosphamidon	50
Dicrotophos	50
Mevinphos	50
Naled	50
TEPP	50
Dimethoate	25
Monocrotophos	25
Acephate	25
Trichlorphon	10
Methamidophos	10
B. Phenyl Derivatives	
EPN	1×10^3
Carbophenothion	1×10^3

	K_d
Dicapthon	5×10^2
Fenthion	5×10^2
Parathion ethyl	5×10^2
Parathion, methyl	3×10^2
Ronnel	2×10^2
Stirofos	2×10^2
Chlorothion	2×10^2
Famphur	2×10^2
Dyphonate	2×10^2
Ciodrin	1×10^2
Crufomate	1×10^2

C. Heterocyclic Derivatives

Chlorofenvinphos	5×10^2
Phosalone	5×10^2
Imidan	5×10^2
Azinophosethyl	1×10^2
Azinophosmethyl	1×10^2
Diazinon	50
Methidathion	50
Chlorpyrifos	50

Rationale: The phosphate-based pesticides range from large, complex molecules to relatively small. All have polar moieties ranging in activity from simply electron-rich heteroatoms to reasonably strong acidic hydrogens and basic moieties (e.g., heterocyclic nitrogens). As a result, the pesticides themselves show a wide range adsorption strength.

Limited literature references are available. Strong binding to soils was reported for chlorofenvinphos, carbophenothion, dioxathion and dichlofenthion (Inch, et al., 1972), azinophosmethyl (Helling, 1971), and for malthion (Konrad, et al., 1969). K_d values observed for parathion include 76 (Saltzman, et al., 1972), about 120 (Bowman and Sans, 1977), and 500 (Leenheer and Ahlrichs, 1971).

CARBONATE PESTICIDES

A. Methyl carbonates

	K_d
Bux (metalkamate)	5×10^2
Carbonfuran	5×10^2
Carbaryl	5×10^2
Propoxur	1×10^2
Methiocarb	1×10^2
Mexacarbate	1×10^2
Aminocarb	1×10^2
Chlorpropham	1×10^2
Propham	50
Benomyl	10
Karbutilate	2

B. Thiocarbamates

Thiram	5×10^2
CDEC	5×10^2
Butylate	5×10^2
Vernolate	1×10^2
EPTC	1×10^2
Molinate	50

Rationale: The carbonate (urethane) moiety is relatively polar and contributes markedly to the greater solubility and reduced adsorption of these compounds compared to the organochlorine pesticides. Unfortunately, few fundamental parameters are readily available for these compounds, nor have extensive adsorption data been reported.

Octanol-water partition coefficients for a number of simple analogs are all about four orders-of-magnitude less than DDT (Leo et al., 1971), indicating their low adsorption potential. Values of K_d for carbaryl (= 125; Leenheer and Adhlrichs, 1971), benomyl (= 4.5; Austin and Briggs, 1976), and propham (= 51; Briggs, 1969) have been reported. The relative adsorption of some thiocarbamates has been reported by Gray and Weienrich, (1968).

AMINE AND ANILINE PESTICIDES

Pesticide	K_d
Diphenamide	1×10^2
Pronamide	50
Alachlor	50
Propachlor	50
Propanil	10
Carboxin	10
Bensulide	5

Rationale: The amide pesticides are chemically similar to the carbonates and should exhibit similar adsorption characteristics. There are generally smaller molecules than the carbamates but this factor should be compensated by the reduced number of polar consitutents. The less adsorptive amides have N-H groups which should hydrogen bond with water molecules.

NTIROANILINE PESTICIDES

Pesticide	K_d
Phenoxalin	1×10^3
Butralin	5×10^2
Profluralin	5×10^2
Trifluralin	5×10^2
Benefin	5×10^2
Fluchloralin	1×10^2
Dinitramine	50
Nitralin	50

Rationale: The nitroanilines contain relatively few non-conjugated polar groups to contribute to electrostatic interactions. Being quite large molecules, hydrophobic interactions should be strong, resulting in large K_d's which are primarily dependent on the size of the substitution.

The ranking presented is supported by adsorption studies on soils (Harvey, 1974) The high K_d values are indicated in soil adsorption studies by Helling (1971), Majka and Lavy (1977), and Grover (1974). K_d values of 1.6×10^3 and 2.8×10^3 have been reported for profluralin and butralin, respectively (Carringer, et al., 1975); but these values were based on adsorption on pure soil organic matter and thus are probably higher than would be representative of "average" soils and sediments.

TRIAZINE PESTICIDES

Pesticide	K_d
Prometome	8
Ametryne	8
Simazine	6
Atrazine	5
Cyanazine	3
Propazine	1
Metribuzin	1
Aminotriazole	1

Rationale: The triazine herbicides are all compact molecules containing at least one polar-ionizable group, usually amino-hydrogens, available to hydrogen bond with water. As a result, these herbicides are quite soluble and exhibit low adsorption on soils.

The ranking presented above has been observed in soil adsorption studies by Helling (1971) and Rogers (1968). Hurle and Freed (1972) reported K_d values of 2.2. to 4.3 and 4.1 to 8.2 for atrazine and simazine, respectively, on silt loam. Average K_d values for adsorption by 25 soils were reported to be: propazine, $K_d = 2.0$; atrazine, $K_d = 2.7$; simazine, $K_d = 3.7$; and prometone, $K_d = 7.8$ (Talbert and Fletchall, 1965). K_d values of approximately 4 were reported for both cyanozine and atrazine (Majka and Lavy, 1977), while K_d for atrazine have also been noted at about 2.8 (Dao and Lavy, 1978). Liu _et_ _al._ (1970) observed K_d values for ametryne ranging from 2 to 10, depending primarily on the amount of organic matter in the soils. The latter authors reported a K_d for ametryne of approximately 150 for a muck (very high organic content) soil.

ORGANIC ACID PESTICIDES

		K_d
A.	Aliphatic Acids and Esters	
	Glyphosate	0.2
	Trichloroacetic Acid	0.2
	Dalapon	0.2
B.	Aromatic Acids and Esters	
	Bifenox	0.5 - 1
	Chloramben	0.5 - 1
	Dicamba	0.5 - 1
	DCPA	0.5 - 1
	Fenac	0.5 - 1
	Naptalam	0.5 - 1
	Picloram	0.5 - 1
	propargite	0.5 - 1
C.	Phenoxy Compounds	
	Erbon	1×10^2
	2,4-D	1.0
	MCPA	1.0
	2,4,5-T	2.0
	Silvex	2.0
	Dinoseb	10
	Endothall	0.2

Rationale: The organic acid pesticides are treated together since they share the common feature that, with few exceptions, the activity of the carbonic acid moiety is sufficient to make these compounds readily soluble and to exhibit minimal adsorption. The two exceptions to this generalization are dinoseb, a weakly-acidic phenol, and erbon, an ester. Both of these latter compounds should show increased adsorption due to strong hydrophic interactions not countered by solibilizing hydrogen or ionic bonding.

The low adsorption of these compounds have been reported for dicamba, picloram, fenac and 2,4-D (Helling, 1971); picloram (Farmer and Aochi, 1974; Gaynor and Volk, 1976; Grover, 1971; Davidson and McDougal, 1973); 2,4,5-T (O'Connor and Anderson, 1974); 2,4-D (Grover, 1973); picloram and 2,4-D (Khan, 1973); picloram and 2,4,5-T (Majka and Lavy, 1977); dicamba, picloram and 2,4-D (Grover, 1977); and dicamba (Garringer, et al., 1975).

UREA PESTICIDES

Pesticide	K_d
Chloroxuron	5×10^2
Chlorbromuron	2×10^2
Linuron	1×10^2
Diuron	1×10^2
Monuron	50
Fluometuron	20
Fenuron	10

Rationale: The urea pesticides are chemically similar to the carbamate and amide pesticides and show the same range of K_d values. The molecules are not small, but polar and hydrogen bonding moieties (N-H and C=O) decrease the aqueous activity.

A relatively large number of studies have been reported for these compounds. The results are summarized below as a table of observed K_d values in soils. The references are indicated by the numbers in parentheses and are noted at the end of the table.

Pesticide	K_d
Chloroxuron	40-110(2); 650(4)
Chlorbromuron	217(5)
Linuron	50-250(2); 10.2-15(3); 210(4); 154(5)
Diuron	85-12(3); 70(4); 94(5)
Monuron	33(4); 29(5)
Fluometuron	22(5)
Fenuron	15(4)

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(1) Geissbuhler, et al., 1963

(2) Hance, 1971

(3) Hurle and Freed, 1972

(4) Lambert, 1967

(5) Briggs, 1969

Miscellaneous Pesticides

The miscellaneous pesticides are presented in the order they were provided by Battelle. The name of the compound is followed by the estimated K_d values. Any supporting literature references are indicated by numbers which refer to the list following the table.

Pesticide	K_d
Allethrin	1×10^4
Pyrethrum	1×10^4
Rotenone	1×10^3
CMA	0.2
DSMA	0.2
MSMA	0.2
Bentazon	0.2(1)
Bromacil	5(2)
Pyrazon	30(3,4)
Terbacil	50(2)
Diquat	5×10^3(5)
Paraquat	5×10^3(6,7)
Chlorothalonil	50
Dichlobenil	20 (8)
Copper Napthalate	5×10^2
Fenbutalin Oxide	
Mancozeb	5
Acrolein	0.2

Pesticide	K_d
Captan	30
Difolatan	50
Dinitrobutyl Phenol	50
Dodine	0.5
Methazole	5
Methomyl	5
Methyl Bromide	10
Norflurazon	50

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1. Abernathy and Wax, 1973
2. Rhodes, _et al._, 1970
3. Fusi, _et al._, 1976
4. Jamet et Marie - Andree Piedallu, 1975
5. Helling, 1971
6. Damanakis, _et al._, 1970
7. Burns, _et al._, 1973
8. Furmidge and Ogersby, 1967

APPENDIX C REFERENCES

Abernathy, J.R., and L. M. Wax. 1973. "Bentazon Mobility and Adsorption in Twelve Illinois Soils." *Weed Sci.* 21:224-227.

Adamson, A. W. 1976. *Physical Chemistry of Surfaces.* John Wiley and Sons. New York. 698 pp.

Austin, D. J., and G. G. Briggs. 1976. "A New Extraction Method for Benomyl Residues in Soil and its Application in Movement and Persistence Studies." *Pestic. Sci.* 7:201-210.

Bailey, G. W., and J. L. White. 1970. "Factors Influencing the Adsorption, Desorption and Movement of Pesticides in Soils." *Res. Rev.* 32:29-92.

Boucher, F.R., and A. F. Lee. 1972. "Adsorption of Lindane and Dieldrin Pesticides on Unconsolidated Aquifer Sands." *Environ. Sci. Technol.* 6:538-543.

Bowman, B. T., and W. W. Sans. 1977. "Adsorption of Parathion, Fenitrothien, Methyl Parathion, Aminoparathion and Paroxon by Na$^+$, Ca^{2+}, and Fe^{3+} Montmorillonite Suspensions." *Soils Sci. Soc. Amer. J.* 41:514-519.

Briggs, G. G. 1969. "Molecular Structure of Herbicides and Their Sorption by Soils." *Nature.* 223:1298.

Burns, R. G. and L. J. Andrus. 1970. *Weed Res.*, 10:49-57.

Burns, I.G., H. H. Hayes, and M. Stacey. 1973. "Physicochemical Interactions of Paraquat with Soil Organic Materials and Model Compounds. 2. Adsorption and Desorption Equilibria in Aqueous Suspensions." *Weed Res.* 13:79-90.

Carringer, R. D., J. B. Weber, and T. J. Monaco. 1975. "Adsorption-Desorption of Selected Pesticides by Organic Matter and Montmorillonite." *J. Agr. Food Chem.* 23:568-572.

Christman, R. F., and R. A. Minear. 1971. "Organics in Lakes." In S. J. Faust and J. V. Hunter (Eds.), *Organic Compunds in Aquatice Environments.* Marcel Dekker, New York. pp. 119-143.

Damanakis, M., D. S. H. Drennan, J. D. Fryar, and K. Holly. 1970. "The Adsorption and Mobility of Paraquat on Different Soils and Soil Constituents." *Weed Res.* 10:164-227

Dao, T. H., and T. H. Lavey. 1978. "Atrazine Adsorption on Soil as Influenced by Temperature, Moisture Content and Electrolyte Concentration." *Weed Sci.* 26:303-308.

Davidson, J. Mr., and J. R. McDougal. 1973. "Experimental and Predicted Movement of Three Herbicides in a Water Saturated Soil." J. Environ. Qual. 2:428-433.

Donigan, A. S. Jr., D. C. Beyerlein, H. H. Davis, Jr. and N. H. Crawford. 1977. "Agricultural Runoff Management (ARM) Model Vertion II: Refinement and Testing." U.S. Environmental Protection Agency Report No. EPA-600/2-77-098, US EPA, Environmental Research Laboratory, Athens, Georgia. 293 pp.

Dexter, R. N. and S. P. Pavlor. 1978. "Distribution of Stable Organic Molecules in the Marine Environment: Physical Chemical Aspects. Chlorinated Hydrocarbons," Marine Chem., in press.

Farmer, W. J., and Y. Nochi. 1974. "Picloram Sorption by Soils." Soil Sci. Soc. Amer. Proc. 38:418-423.

Frank, H.S., and M. W. Evans. 1945. "Free Volume and Entrophy in Condensed Systems. III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electolytes." J. Chem. Phys. 13:507-532.

Franks, F. 1975. "The Hydropholic Interaction." In F. Franks (Ed.). Water: A Comprehensive Treatise. Vol. 4a. Plenum Press, New York. pp. 3-801.

Furmidge, C. C., and J. M. Osgerby. 1967. J. Sci. Food Agr. 18:269-173.

Fusi, P., S. Ceconni, M. Franci, and C. Vazzana. 1976. "Adsorption et Desorption de la Pyrazone par Quelques Collorides Organiques et Nunreaux." Weed Res. 16:101-109.

Gaynor, J.D., and V. V. Volk. 1976. "Surfactant Effects on Picloram Adsorption by Soils." Weed Sci., 24:549-552.

Geisshihler, H., C. Haselbach, and H. Aebi. 1963. "The Fate of N-(4-Chlorophenoxy)-Phenyl-N,N-Dimethylurea (C-1983) in Soils and Plants." Weed Res. 3:140-153

Gray, R.A., and A. J. Weirich. 1968. "Leaching of Five Thiocarbanate Herbicides in Soils." Weed Sci. 16-77-79.

Grover, R. 1973. "The Adsorptive Behavior of Acid and Ester Forms of 2,4-D on Soils." Weed Res. 13:51-58.

Grover, R. 1971. "Adsorption of Picioram by Soil Colloids and Various Other Adsorbents." Weed Sci. 19:417-418.

Grover, R. 1977. "Mobility of Dicamba, Picioram and 2,4-D in Soil Columns." Weed Sci. 25:259-162.

Grover, R. 1974. "Adsorption and Desorption of Trifluralin, Triallate and Diallate by Various Adsorbents." *Weed Sci.* 22:405-408.

Hamaker, J. W., and J. M. Thompson. 1972. "Adsorption". In C. A. Goring and J.W. Hamaker (Eds.). *Organic Chemicals in the Soil Environment, Vol. 1*, Marcel Dekker, New York. pp.49-143.

Hance, J.C. 1971. "Complex Formation as an Adsorption Mechanism for Linuron and Atrazine." *Weed Res.* 11:106-110.

Harvey, R. 1974. "Soil Adsorption and Volatility of Dinitroaniline Herbicides." *Weed Sci.*, 22:120-134.

Helling, C. S. 1971. "Pesticide Mobility in Soils III. Influence of Soil Properties." *S. Sci. Soc. Amer. Proc.* 35:743-748.

Huang, J. C., and C. S. Liao. 1970. "Adsorptives of Pesticides by Clay Minerals," *J. San. Eng. Div., Proc. Amer. Soc. Civil Eng.*, 96:SA5, 1057-1064.

Hurle, K. B., and V. H. Freed. 1972. "Effects of Electrolytes on the Solubility of Some 1,3,5-Triazines and Substituted Ureas and Their Adsorption on Soils." *Weed Res.* 12:1-10.

Inch, T. D., R. V. Levy, and D. Utley. 1972. "The Mobility of Some Organophsphorus Sheep Dip Insecticides in Soil." *Pestic. Sci.* 3-242-253.

Jamet Et Marie-Andree Piedallu, P. 1975. "Etude de l'adsorption et de la Desorption de la Pyrozone (Amino - 5 Chloro - 4 Pheny (-2,2H Pyridazinone-3) par Differents Types de Sols." *Weed Res.* 15:113-121.

Khan, S.U. 1973. "Interaction of Humic Acid with Chlorinated Phenoxyacetic and Benzoic Acids." *Envir. Letters.* 4:141-148.

Knight, B. A. G. and T. E. Tomlinson. 1970. In *Sorption and Transport Processes in Soils*, Soc. Chem. Ind., London, p. 54-77.

Kononova, M. M. 1966. *Soil Organic Matter* (translated by T. Z. Nowakowski and A.C.D. Newman, Pergamon Press, New York).

Konrad, J., G. A. Chesters, and D. E. Armstrong. 1969. "Soil Degradation of Malthion, a Phosphorodithieate Insecticide." *Soil Sci. Soc. Amer. Proc.* 33:259-262.

Lambert, S. M. 1967. "Functional Relationships Between Adsorption in Soil and Chemical Structure." *J. Agr. Food Chem.* 15:572-575.

Leenheer, J. A. and J. L. Ahlricks. 1971. "A Kinetic and Equilibrium Study of the Adsorption of Carbaryl and Parathion Upon Soil Organic Matter Surfaces." *Soil Sci. Soc. Am. Proc.* 35:700-705.

Leland, H. V., W. N. Bruce, and N. F. Shimp. 1973. "Chlorinated Hydrocarbons Insecticides in Sediments of Southern Lake Michigan," Environ. Sci. Technol., 9:883-838.

Leo, A., C. Hansch, and D. Elkins. 1971. "Partition Coefficients and Their Uses." Chem. Rev. 71:525-616.

Liu, L.C., H. Cibes-Viode, and F.K.S. Koo. 1970. Adsoption of Dimetryne and Diron by Soils." Weed Sci., 13:470-474.

Lotse, E. G., D. A. Graetz, G. Chesters, G. F. Lee, and L. W. Newland. 1968. "Lindane Adsorption by Lake Sediments." Environ. Sci. Technol. 2:353-357.

Majka, J.T., and T. L. Lavy. 1977. "Adsorption, Mobility and Degradation of Cyanazine and Diuron in Soils." Weed Sci. 25:401-406.

Morrison, R. T., and R. N. Boyd. 1966. Organic Chemistry. Allyn and Bacon, Boston. 1204 pp.

Neihof, R. A. and G. I. Loeb. 1972. "The Surface Charge of Particulate Matter in Seawater." Limnol. Oceanogr. 17:7-16.

O'Conner, G. A. and J. U. Anderson. 1974. Soil Factors Affecting the Adsorption of 2,4,5-%. Soil Sci. Soc. Amer. Proc. 38:433-436.

Pavlou, S. P., R. N. Dexter, and J. R. Clayton. 1974. "Chlorinated Hydrocarbons in Coastal Marine Ecosystems." In Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems, May 1-3, 1974, Ottawa, Canada. pp. II-31-II-35.

Rogers, E. H. 1968. "Leaching of Seven S-Triazgines." Weed Sci. 26:117-121.

Rhodes, R.C., I. J. Belasc, and H. L. Pease. 1970. J. Agr. Food Chem. 8:524-529.

Saha, J. G., B. Bharati, Y. W. Lee and R. L. Randall. 1969. J. Agr. Food Chem., 17:877-893.

Saltzman, S., L. Kliger, and B. Yaron. 1972. "Adsorption-Desorption of Parathion as Affected by Soil Organic Matter." J. Agr. Food Chem. 20:1223-1226.

Shin, Y. O., J. J. Chordan, and A. R. Wolcott. 1970. "Adsorption of DDT by Soil Fractions and Biological Materials." J. Agr. Food Chem. 18:1129-1133.

Talbert, R. E., and O. H. Fletchall. 1965. "The adsorption of Some S-Triazgines in Soils." Weed Sci. 13:-46-49.

*U.S. GOVERNMENT PRINTING OFFICE: 1982-559-092/3401

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